JPL PUBLICATION 79-63

Novel Approaches for Alleviation of Electrical Hazards of Graphite-Fiber Composites

Kumar Ramohalli

October 15, 1979

National Aeronautics and
Space Administration

Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California

TECHNICAL REPORT STANDARD TITLE PAGE

1. Report No. JPL Pub. 79-63	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle Novel Approaches for Alleviation of Electrical Hazards of Graphite-Fiber Composites		5. Report Date October 15, 1979 6. Performing Organization Code
7. Author(s) Kumar Ramohalli		8. Performing Organization Report No.
9. Performing Organization Name and Address JET PROPULSION LABORATORY California Institute of Technology 4800 Oak Grove Drive Pasadena, California 91103		10. Work Unit No. 11. Contract or Grant No. NAS 7-100 13. Type of Report and Period Covered JPL Publication
12. Sponsoring Agency Name and Address NATIONAL AERONAUTICS AND SPACE ADMINISTRATION Washington, D.C. 20546		14. Sponsoring Agency Code
15. Supplementary Notes		

16. Abstract

This study was aimed at exploring the feasibility of different approaches to solve the electrical problems posed by graphite-fiber composites. Four basically different approaches were considered: gasification of fibers, retention in the matrix, clumping to prevent entrainment, and electrical insulation of fibers. The techniques used to achieve them are described in some detail. These involved surface treatment of fibers to improve the wettability of fibers and coating the fibers with the selected substances before laying them up for composite fabrication. Thermogravimetric analyses were performed on the plain and treated fibers in inert (nitrogen, argon) and reactive (air) atmospheres. The treated fibers embedded in epoxy were ignited in a Bunsen flame to determine the efficiency of these treatments. A simple apparatus was assembled to detect the time for the first short circuit (in a typical electrical circuit) when exposed to the combustion products from a graphite fiber composite fire. The state-of-the-art and treated fibers cast in typical epoxy were burned and ranked for potential success. It was inferred that the gasification schemes appear promising when reduction or oxidation is tried. It was also found that some very promising candidates were available for the clumping and for the electrical insulation of fibers. The description of a plan for future work in this area concludes this report.

17. Key Words (Selected by Author(s))	18. Distribution Statement
Air Transportation and Safety Chemical Engineering Materials (General) Composite Materials Fibers and Textiles	Unclassified - Unlimited

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price
Unclassified	Unclassified	42	

JPL PUBLICATION 79-63

Novel Approaches for Alleviation of Electrical Hazards of Graphite-Fiber Composites

Kumar Ramohalli

October 15, 1979

National Aeronautics and
Space Administration

Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California

The research described in this publication was carried out by the Jet Propulsion Laboratory, California Institute of Technology, under NASA Contract No. NAS7-100.

ABSTRACT

This study was aimed at exploring the feasibility of different approaches to solve the electrical problems posed by graphite-fiber composites. Four basically different approaches were considered: gasification of fibers, retention in the matrix, clumping to prevent entrainment, and electrical insulation of fibers. The techniques used to achieve them are described in some detail. These involved surface treatment of fibers to improve the wettability of fibers and coating the fibers with the selected substances before laying them up for composite fabrication. Thermogravimetric analyses were performed on the plain and treated fibers in inert (nitrogen, argon) and reactive (air) atmospheres. The treated fibers embedded in epoxy were ignited in a Bunsen flame to determine the efficiency of these treatments. A simple apparatus was assembled to detect the time for the first short circuit (in a typical electrical circuit) when exposed to the combustion products from a graphite fiber composite fire. The state-of-the-art and treated fibers cast in typical epoxy were burned and ranked for potential success. It was inferred that the gasification schemes appear promising when reduction or oxidation is tried. It was also found that some very promising candidates were available for the clumping and for the electrical insulation of fibers. The description of a plan for future work in this area concludes this report.

FOREWORD

This report presents the results from a four-week (March 1978) effort of the Solid Propulsion and Environmental Systems Section at the Jet Propulsion Laboratory, California Institute of Technology. Contributors included Kumar Ramohalli, Warren Dowler, William Mueller, James Quinn, Donald Udlock, Giulio Varsi, Lien Yang and Fred Tervet.

The funding was provided by Code RW (RT) at National Aeronautics and Space Administration Headquarters. Messrs. Bernard Achhammer, George Deutsch and Dell Williams were the Program Managers.

CONTENTS

Figures

Figures

Table

SECTION I

INTRODUCTION

Electrical problems have been reported in the processing and use of graphite fiber composites (Refs. 1 to 3). As was evident at the workshop on Modified Composite Materials (held at NASA Langley Research Center March 23 to 24, 1978), considerable interest exists in graphite fiber composites because of their light weight and high strength. A projection is that approximately one-billion pounds of graphite fibers will be used by 1990 in applications ranging from automobiles to golf clubs. It is evident that this huge industry will be in jeopardy unless the recognized electrical hazards can be overcome economically and without sacrificing the good features. Also, a small departure from the state-of-the-art materials and processes is desired to facilitate quick transfer to industry. Although it was not clear at the time this work started (March 1, 1978), it became clear at the Langley Workshop that a minimum of two years would elapse before a solution can be incorporated into commercial products even if the full solution were available today.

It was the basic aim of this four-week effort to present ideas, backed by results that may be preliminary at this time, that show promise of a solution to the problem. It is our ultimate aim to prevent release of electrically conductive graphite fiber fragments from composites in a fire without compromising the proven good features of these fibers (strength, weight, cost). To achieve these goals, four fundamentally different approaches were considered:

(1) Gasify the fibers so that no conducting fiber fragments will be airborne, scattered, and rendered harmful.

(2) Clump the fibers together so that the fiber fragments would not be airborne, but would settle quickly.

(3) Retain the fibers in the matrix, which may char.

(4) Insulate the fibers so that no electrical hazards are caused even if the fiber fragments are airborne.

Other approaches such as resin modifications, alternate fibers, and secondary fiber inclusions received only minimal thought in this work.

It soon became apparent that some standard test was needed to determine the electrical hazard posed by the graphite fiber composites. The unavailability of standard tests (which was later confirmed at the Langley meeting) prompted an in-house development effort. A simple apparatus was constructed to detect short circuits when a conducting fiber contacted the sensor, a typical circuit board used in electronic equipment. This apparatus evolved into a fairly standard test equipment that gave reproducible results on both the state-of-the-art and modified composites.

The actual tests devised and conducted on the fibers and modifications thereof are described in Section II. The design philosophy, construction, and working of the test apparatus are described in Section III. The results are summarized and areas for future work are identified in Section IV. Practically all of the extensive data tables are presented at the end of the report. It should be mentioned that the processing of these data to yield several interesting chemical and physical constants will be pursued when the work is continued. Also, this work has yielded a host of scanning electron microscope pictures of plain, treated, and unburned and burned fibers. Many of them are also presented at the end of the report. These have the important purpose of visually transmitting information on the wettability, uniformity of fiber surface treatment, and the resin-fiber interface before and after a typical burn test.

SECTION II

THE EXPERIMENTAL WORK

The basic objective of these experiments was to quickly assess the potential of many fiber modifications to gasify the fibers in a fire. It was the secondary aim to pursue to a lesser extent the other three areas also. Here, the objective was to quickly assess the potential of fiber modifications to retain the fibers in the resin char, clump the fibers to prevent the occurrence of airborne fiber fragments, and to electrically insulate the fibers with novel metal cladding techniques. The thermogravimetric analyzer and the simple propane (or natural gas) flame were used to determine the thermal degradation and the burning characteristics of the state-of-the-art and modified graphite fiber composites. It should be mentioned that a thermochemical model developed earlier at JPL successfully relates the thermal degradation behaviour at relatively low temperatures (DSC, TGA data) to actual burning at high temperature in flames. This model can interpret coherently a host of seemingly inconsistent data on thermal-oxidative degradation of plastics and, further, can predict the burn rates of composite materials using purely the fundamental physicochemical property values of the ingredients; this is considered by several investigators to be a major step toward solving the problem of burning composites. The main point of the above comment is to note that the TGA data are very relevant to actual burn rate data and tests, contrary to what a superficial examination may suggest.

Unless otherwise stated, graphite fiber (Fig.1) in this report refers to Thornel 300 strands kindly sent to us by Mr. Robert Jewel of NASA Langley Research Center. This material was thought to be representative of the many varieties of graphite fibers in use today, at least for the purposes of initial tests to demonstrate the feasibility of modifications to alleviate the electrical hazards. The resin is also one of the typical epoxies. Although various forms of epoxies and polyimides are used today, RF-3000 hardened by RF-61[1] was thought to be a reasonably representative epoxy, at least for our purposes of feasibility demonstrations. It is possible that some of the numerical values reported here would change a little when different varieties of graphite fibers and resins are used. However, it would be very surprising if the basic conclusions of this report were altered by the results of tests using such different materials.

---

[1]Manufactured and supplied by E.V. Roberts Associates, Culver City, CA.

SECTION III

THE TESTS

A. GASIFICATION APPROACH

Two approaches were considered under this subtask. oxidation and reduction.

1. Oxidation

Since the surface temperature of combustion (fast oxidation) of graphite is in the vicinity of 1300°C, fast oxidation of graphite is hardly reached by the simple combustion of a composite panel, which occurs at typical surface temperature of 400 to 500°C. Also, even if the requisite temperature are reached, the rates of combustion (oxidation) of the graphite are too low compared to the same rates for the resin. This has the practical implication that the resin burns away fast leaving behind the graphite fibers that do not combust in the absence of the supporting flame. The fiber diameter of 8 μm presents a 2500 cm^2 surface area per gram of mass. This is very large and leads to rapid heat loss and is conducive to early extinction even if combustion is initiated.

It is precisely under these conditions that a catalyst is best applied. Sodium, even in trace quantities is known to enhance the oxidation of graphite (Ref. 4). Hence the incorporation of sodium into the graphite fibers was thought to enhance oxidation rates in a fire situation. The thought also arose that some of the more electronegative alkali metals (potassium, lithium) may be catalysts too. Hence the following were selected as oxidizing salts of these alkali metals:

(1) Sodium silicate.

(2) Potassium silicate.

(3) Potassium perchlorate.

(4) Potassium nitrate.

(5) Sodium nitrate.

(6) Lithium nitrate.

(7) Sodium bicarbonate.

(8) Sodium carbonate

(9) Potassium permanganate

It was expected that these salts would not only catalyze the reaction, but would also supply some of the oxygen needed for oxidation.

At this primary stage, the graphite fibers were dipped into a diluted solution of these salts and ambient dried (Fig. 2). It was

found that etching with an argon arc plasma greatly improved the wettability (Fig.3). The coated fibers were degraded in a TGA apparatus and also burned in a laboratory Bunsen flame. The coated fibers were examined under a scanning electron microscope; also X-ray spectra were obtained to verify the uniformity and thickness of coatings. The results from the TGA are being processed to yield the activation energy and the preexponential constant for an assumed first-order reaction of graphite pyrolysis. An example is shown in Fig. 4.

The results of the burn tests in the open Bunsen flame can only be qualitative. Nevertheless the time for complete disappearance of a bundle (300 strands) of fibers can be used as a quantitative guide to assess the effectiveness of the treatment. The results indicate that the oxidation rates are affected little by these techniques. It is obvious that more effective catalysts are needed; it is also possible that the catalyst application has to be improved.

One of the principal difficulties with the oxidative gasification of graphite is that quite large quantities of oxygen are needed. Twelve grams of carbon need a minimum of sixteen grams of oxygen for oxidation (to carbon monoxide which may subsequently get oxidized to carbon dioxide in air). Private communications with leading investigators in the combustion field revealed no known catalysts for the oxidative gasification of graphite, under the present case.[2]

2. Reduction

It was then thought possible to gasify carbon with a reduction reaction. The high volatility of many hydrocarbons is well known. If the graphite fiber could be transformed into a suitable hydrocarbon at the combustion temperature of the composite material, gasification could be readily accomplished. This hydrogenation reduction has the advantage that, at least theoretically, twelve grams of graphite need only one gram of hydrogen for gasification (if the process converts graphite into benzene (C_6H_6)-like substances).

The idea here is to retain (adsorb) hydrogen in (on) the graphite fibers so that the good mechanical properties and chemical stability are not lost in the normal service environment. To achieve this aim, it is necessary to incorporate hydrogen into graphite. Two of the metals known for their great adsorptivity (of hydrogen) are zirconium and palladium. Although palladium is very expensive, it was readily available in small quantities at JPL and was sputtered onto the graphite fibers by means of a gas discharge. The mass addition due to this palladium layer was indiscernible. The palladium sputtered graphite fibers were kept in a hydrogen tank for 10 to 30 minutes at 68 atmospheres of pressure at atmospheric temperature (70°C). These fibers were then subjected to the same TGA burn tests mentioned earlier.

---

[2] Subsequent work at JPL (June 1978) has revealed several powerful catalysts for the gasification of these fibers. Many patent disclosures have been made, and the results will soon be published.

Although the TGA data (see Appendix for examples of data) have not yet revealed a significant difference from the earlier mentioned data, the burn tests showed that the palladium/hydrogen treated fibers burned out in about one-third (1/3) the time needed for the disappearance of the untreated graphite fibers (shown in Table 1).

This indicates that the hydrogenation scheme, although very preliminary at this stage, is worthy of further pursuit.

B. RETENTION OF FIBERS IN MATRIX

The basic intention of this approach was to have some form of a coating on the fiber that would cross-link with the fiber at one end and with the resin char at the other, thereby retaining the fibers in the matrix of the composite char. Past experience at JPL had shown that the restrictor paste used in solid propellant combustion formed an excellent charring coat in certain applications (Ref. 5).

As a first try, this paste was used to coat the graphite fibers. This restrictor paste consists of 10-percent ethylcellulose and 3-percent tricresylphosphate in 87% methyl ethyl ketone. The previously mentioned tests were repeated on these treated fibers also.

In addition, these fibers were also cast in a typical resin (epoxy). The results of burning this material are shown in Table 1. These graphite fiber composites were tested for possible electrical shorts when burned. The apparatus (described later) was used to determine the time taken for the first short circuit caused by the landing of an electrically conductive graphite fiber fragment on an exposed circuit. These tests became a standard feature for all the modified composite materials in this program. Test results showed that the time to the first short circuit caused by burning the state-of-the-art graphite fiber/epoxy composites was consistently 12 seconds. No shorts were observed at all from burning graphite fibers with silicate coatings in tests lasting longer than 60 seconds. It may be seen that the coating of the graphite fibers with the restrictor paste prolongs this time to 150 percent. While this is not yet an acceptable solution (it is necessary to prolong the time to infinity) the improvement again leads us to conclude that the idea is worthy of further pursuit. Other chemicals and concentrations may solve the problem completely.

C. CLUMPING OF FIBERS TO AVOID AIRBORNE FRAGMENTS

It was basic aim of this approach to investigate coatings (on graphite fibers) that would, in a fire, coalesce the fibers, clump them and prevent entrainment. Coats that form a glassy layer upon being heated are the obvious choices here. The following chemicals were chosen for the first attempt:

(1) Sodium silicate.

(2) Potassium silicate.

(3) Borosilicate glass.

(4) Control 64 (a vinyl wallcovering adhesive).

Again, solution dipping was the method employed for the coat application.

Three separate coatings for Thornel-300 graphite fibers have been investigated. They are sodium silicate ($NaSiO_3$-$9H_2O$ or $Na_2Si_3O_7$), Borosilicate glass, and Control 64[3]. The fiber coating technique, testing, and results obtained will be discussed for each coating.

1. Fiber Coating

The sodium silicate coatings were prepared as follows. Solutions of sodium silicate ($NaSiO_3$-$9H_2O$) were prepared by dissolving the desired amounts in distilled water at room temperature (≈25°C). The fibers were coated by immersing a fiber bundle into the solution for two to three seconds. Upon removal from the solution, the fibers were dragged over the lip of the solution container to remove excess solution. The coated fiber bundles were then dried in a horizontal position in a vacuum oven at 105°C. In ten minutes the fibers were dried to constant weight. The coating thickness (% weight gain) varied considerably, even as the solution concentration was held constant. However, as shown in Fig. 2a, the general trend for the percent weight gain to increase with the solution concentration.

The second coating material was Kimble CV-101 powdered glass. This is a borosilicate glass that softens at 425°C. The glass was applied to the fibers by vacuum deposition. The graphite fibers were taped onto an aluminum disc, approximately 15 mm above the powdered glass. The deposition conditions were: current 100 mA, pressure ≈13.33 N/m^2 (≈100 mtorr), time = 15 minutes.

The third coating, Control 64, was applied in much the same manner as was the sodium silicate. Since this material is not completely soluble in water, the mixtures were stirred to prevent settling. Figure 2b shows the percent weight gain of mixture concentration (percent Control 64 in distilled water) for the five used. In the one labeled "settled", the mixture was allowed to stand, and the fibers were dipped in only the clear solution above the settled material.

2. Epoxy Resin Coating

Fibers which were coated, and uncoated (control) fibers were mixed with an epoxy resin to prepare a composite for subsequent burning experiments. In all cases, the epoxy used was an 80/20 mixture of RF-3000/RF-61.[4]

---

[3]A vinyl wallcovering adhesive manufactured by Control Products, Redondo Beach, California

[4]Manufactured by E. V. Roberts Associates, Culver City, California.

This resin was applied to the fiber bundle with a spatula, then worked into the fibers with the hand. All excess resin was then squeezed out. This provided samples in which the resin content ranged from 45 to 60 percent, with the average being around 50 percent. The epoxy was then cured for a minimum of 2-1/2 hours at 60°C.

3. Burning Tests

Two types of burning tests were conducted. Each involved the use of a propane torch. The flame was adjusted so that the light blue portion of the flame was approximately 25 mm long. The fibers were held so that the end of the fiber bundle was about one to two millimeters above the tip of the light blue portion of the flame. The point at which the two types of burning tests differ is in the analysis for escaping fibers during the exposure to the flame. In the first test, only a visual examination was made. It was very easy to determine visually if many, a few, or none of the glowing fibers left the bundle. In the second test, the escaping fibers were drafted up a 75-mm-diameter glass cylinder and across the bar grid of the electrical detector described later. The time interval from ignition to the detection of the first electrical short was measured as an indication of electrical hazard. The escaping fibers would short on the grid, and cause a light to come on. In this test, the time required to short the grid was used as an indicator of escaping fibers.

4. Results and Discussion

Sodium silicate coated fibers, which had been mixed with an epoxy to form a composite, were exposed to the propane flame and analyzed by each of the two techniques described. Visual observations of bundles in a propane flame yielded no evidence of escaping fibers, regardless of the amount of coating, which ranged from 2 to 23.6 percent. Similar results were obtained when the test indicator was the electrical grid. With a 2-percent sodium silicate coating, no electrical shorts were ever recorded, indicating that no graphite fibers escaped from the burning composite. What appears to happen is that the graphite fiber bundle becomes "glued" together while in the flame. After 60 to 70 seconds, the bundle would break off where it was held and fall to the bench top below, in one piece. Control samples, identical in every way except they contained no sodium silicate coating, typically would short the electrical grid in 10 to 20 seconds, with the average being around 12 seconds.

To better determine why no fibers escaped from the sodium silicate coated fiber bundles, an investigation of unburned fibers, both coated with sodium silicate and uncoated, with a scanning electron microscope (SEM) was undertaken.

Figure 5 shows photographs of Thornell 300 graphite fibers coated with sodium silicate before and after burning. With this high level of coating (13.7%), the sodium silicate is clearly visible; with a lower percentage coating, the unburned fibers appear much like uncoated fibers. However, after exposure to the flame, a dramatic change has taken place. The coating has melted, and adhered to or bridged across

neighboring strands and bonded them together. This bonding is the mechanism that prevents fibers from escaping during exposure to a flame. X-ray scans, included in Fig. 5, clearly indicate the presence of sodium and silicon both before and after burning.

The results obtained with the sputtered-on borosilicate glass are not yet as well defined as those with the sodium silicate, yet they are also encouraging. The percent weight increase resulting from the coating was not measured; however, a slight stiffening of the fiber bundle was noted. The only burning tests made with borosilicate glass-coated fibers were visual; however, in each test no fibers were observed to leave during exposure to the flame. As with the sodium silicate coated fibers, the glowing bundle eventually (in 60 to 70 seconds) fell to the bench top as one unit. Additional tests will have to be made using the borosilicate glass coating to further determine its promise, but these preliminary results are encouraging.

The third coating material tested, Control 64, also yielded encouraging results. Duplicate tests, using fiber-epoxy composites with Control 64 coatings ranging in weight from 2.3 to 185 percent, using the electrical grid produced only one short (14% coating), which could not be repeated. No explanation for this short will be attempted, except that it is expected that this will not be a normal test result since it could not be repeated. SEM photomicrographs of this coating, Fig. 6, show many fractured, rock-like particles all over the fibers, both before and after burning. An EDAX scan showed that there were silicates among the other materials on the fibers. Photomicrographs after burning fail to show evidence of coating melting and/or bonding together of the fibers. The only result of exposure to the flame is that the fiber diameter appears to have decreased. However, the fact remains that, except for one isolated instance among many tests, no fibers escaped during exposure to a propane flame.

D. INSULATING THE GRAPHITE FIBERS

As a drastic departure from dielectric coats, an active metal coat was used. The idea was to keep the good electrical conductivity (needed in many instances) until exposure to a fire when the active metal coat would be oxidized to an insulating layer in the fire. Aluminum has a low melting point (~600°C) so that during the flame exposure it will flow and uniformly coat the fiber rather than disintegrate due to thermal stresses. The aluminum-graphite interface properties are known to be very good from previous studies in other applications (Ref. 6). The vacuum sputtering of aluminum on graphite fibers gave a coating nearly two microns thick (Fig. 7). These coated fibers were cast in the same epoxy system and cured as mentioned before. These composites when burned gave no electrical shorts in the test apparatus. The postfire SEM examination shows uniform aluminum oxide on the fibers (Fig. 8). Thus this technique appears most promising. It has the added advantage that the aluminum oxide possesses considerable mechanical strength. In many instances hollow oxide coatings remained as a shell even when the fibers inside were gasified in the fire (Fig. 9).

SECTION IV

THE TEST APPARATUS

Early in this effort the need was felt for some quantitative test for evaluating the materials for electrical hazards. That is, some test was needed for quantifying the improvement (or degradation) of the modified composite materials in comparison with the state-of-the-art composite materials. Several choices were available. The number of fiber fragments released in unit time could be collected and counted. This would of course require laborious data processing systems. A very much more direct indication of the electrical hazard is given when the electrical problems in typical circuitry in the vicinity of the burning composite are quantified. Also this scheme would serve to rank the several modifications attempted. For the initial effort, a quick screening of test data was needed, but we considered that, if possible, the approach should also be applicable later in obtaining measurements in a controlled test environment such as the National Bureau of Standards smoke-density chamber. The objective of this instrumentation program was to devise and test a technique that could provide data to answer the earlier questions and to provide instrumentation hardware for screening tests of modified graphite fiber composites. It was decided to expose one or more typical electronic circuit boards to the products of burning from a graphite fiber composite. It is worthwhile to remember a few basic numbers in this regard. It was determined that a bundle of graphite fibers from a woven cloth 100 millimeters long has a resistance of about 40 ohms. A single fiber 25 millimeters long has a resistance of about 13,000 ohms. In making these measurements with an ohmmeter, it was determined that the fiber contact resistance would be a major factor that could increase the shorting resistance and thus influence the creation and detection of a short.

Three short detection sensors have been studied: a computer wire-wrap memory load; an interlaced comb grid (Fig. 10) which was to simulate a printed circuit board; and a two-layer interlaced comb grid (Fig. 11), built with 0.48-cm (3/16-in.) -diameter brass rods. The last detector has performed the best because it can let the combustion products of carbon fiber test composites pass through, and it is immune to spurious shorts caused by soot and moisture.

Four fiber-shorting measurement techniques have been investigated: 1) the memory board was subjected to a malfunctions performance test after fiber shorts were created, 2) the detection of the first shorts on the circuit grids by a time delay circuit, 3) the detection of step charges in resistance of the grids, and 4) counting the number of "hits" by coupling through an audio-power transformer connected to the rod grid for a screening test. The time to first short, number 2 above, was selected.

During the testing of some of the materials, it was discovered that mechanical agitation of the burning composite had a determining effect on the fiber fragment release. A pneumatic vibrator (used in many solid-propellant castings at JPL) was used with 6.9×10^4 N/m^2 (10-psi) air pressure as a standard mechanical stimulator. It is estimated that

the frequency of vibration is approximately 1000 Hz at a load of about one g. The flame applied to the composite material also had to be standardized. The flame from a propane torch was used with the inner blue cone 25 mm long. The tip of the blue cone was applied to the composite under test. Lastly, an inverted funnel-chimney arrangement was used over the burning composite to guide the fiber fragments, if any, to the test circuit board. The arrangement, during a test, is shown in Fig. 12. These descriptions complete the mechanical and chemical environment; we next describe the electrical/electronic part.

A. CONDUCTIVE FIBER DETECTOR AND INDICATOR CIRCUITS

Two general types of detector and indicator circuits were designed in the course of this activity, and at least one breadboard of each type was constructed. A functional description of the circuits is presented below. The model breadboard circuit was put on-line operationally during burning tests of carbon fiber samples. The detector circuit designated as Model 2 was characterized in more detail in bench testing, but the breadboard was not completed in time to be used in actual burning tests of carbon fiber samples.

1. Model 1 Detector Circuits

The Models 1 and 1A circuits used in actual burning tests were functionally identical. A block diagram of the circuits is shown in Fig. 13, and photographs of the Model 1A breadboard are shown in Figs. 14 and 15. Schematic details of the Model 1A circuit are shown in Fig. 16.

The central element of the Model 1 circuit is the MC14490 Hex Contact Bounce Eliminator integrated circuit. The intended design application for the MC14490 device is to act as an "interface" element that will provide a clean digital output signal in response to an input signal from bouncing electrical/mechanical contacts much as in a switch or relay. This design function is accomplished in the device by counting four periods of a reference oscillator signal before providing an output in response to an input. As discussed in the data sheet, the oscillator frequency, and hence the signal delay, can be set at any desired value over a relatively wide range by choosing the appropriate value of capacitance that is added externally to the MC14490 device. In application, a 0.2-mf capacitor was used to give an arbitrarily established input-to-output delay of approximately 0.4. seconds.

From the MC14490 data sheet, and as verified by experiment, it was determined that the triggering threshold level of the device is approximately 50 percent of the supply voltage (V_{DD}). The effective input resistance of the device was determined to be approximately 20 kilohms. These parameters, in conjunction with the selected delay time, characterize the response of the detector circuit. That is, when the resistance of the grid sensor reaches a maintained (0.4-second) value of approximately 20 kilohms, the signal indicating LED will be turned on.

In the carbon fiber burning tests, a stop-watch was used to determine the time delay from the start of sample burning to turn-on of the detector circuit LED indicator lamp, which showed that conductive fibers had produced the conditions defined above. As reported elsewhere, measured delay times were in the order of 10 to 20 seconds for untreated fiber samples.

2. Model 2 Detector Circuit

The Model 2 circuit schematic diagram is shown in Fig. 16 and photographs of the breadboard are shown in Fig. 17 and 18. A schematic diagram is available from the author. As mentioned, this circuit was not used in burning tests of carbon fiber samples.

The significant features of the Model 2 detector circuit are (a) the signal load selection capability and, (b) the multilevel resistance limit detectors. Discussing the last of these first, it may seem from the Fig. 16 schematic diagram that six resistance levels are shown by the indicator lamps (L10 through L60). These resistance values (1000-kilohm, 500-ohm) relate to what the grid sensor resistance is when the corresponding lamp lights.

The listed resistance values apply when the R_L load selector switch SW-1 is at the x1 position. The other positions of the switch have multiplication factors that apply to the resistance values listed by the indication lamps. That is, if the switch SW-1 is in the X0.01 position, and if the L10 lamp (only) is on, the grid sensor resistance is 1 kilohm (0.01) X 100 kilohm = 1 kilohm.

The range of the resistance indication at a given load (i.e., the range of 500 ohms to 100 kilohms with R_L = 1 kilohms) was selected based on an examination of oscilloscope data presented.

The indicator circuit has an initial amplifier/buffer stage, designated Ao, with gain of +1, to provide isolation if needed. This stage does not significantly degrade the signal, and does allow for the addition of circuitry that would otherwise adversely load the divider network consisting of the Grid Sensor Resistance (R_{GS}) and the selected load resistance (R_L). Stages A1 through A6 are also op-amp stages, each of which it is desired to detect. For stages A1 through A4, the adjustable calibration resistors are the op-amp feedback resistors; for stages A5 and A6, the adjustable calibration resistors are actually attenuators on the output of the stage, because the overall gain required is close to or less than 1.

Following each op-amp stage is a Schmitt trigger stage that acts as a stable repeatable threshold detector. The Schmitt triggers are also capable of driving the light emitting (LED) indication lamps (L10 through L60).

Calibration of the circuit is done by using various values of fixed resistors connected at the point where the grid sensor would be connected. The calibration need only be done at one position of the load selector switch (most conveniently at the X1 position).

The circuit is presently calibrated such that the indicated resistance (e.g., 100 kilohms) will definitely trigger ST11 and light L10, but a resistance twice that value (200 kilohms) definitely will not trigger ST11; similarly for the remaining stages.

Although this test apparatus was constructed and used as a preliminary screening device in a "quick and dirty" manner, it is heartening to note that at the Langley Workshop no better technique was reported. In fact, considerable interest was expressed by the scientific community in this test technique.

SECTION V

SUMMARY AND FUTURE PLANS

Several important conclusions can be reached from the results of this work. The most significant of these is related to the success of the prevention of electrical hazards and the instrument development. In general, several areas are identified as having great promise if pursued further. The results are summarized under appropriate separate headings.

A. FIBER GASIFICATION

The reduction (hydrogenation) gasification appears novel and promising. The burn time has been decreased by almost a factor of three even with extremely naive hydrogenation schemes. The effect of other hydrogen adsorbing materials should be investigated. The retention of hydrogen in graphite fiber composites over extended periods of service life needs specific investigation. The several chemicals tried for oxidative gasification have met with much less success. It would appear a challenging task to find a suitable catalyst and supply the necessary oxygen for oxidiation.[5]

B. FIBER RETENTION IN MATRIX

The basic idea seems sound. Even the very first chemical (EC and TCP) tried to promote cross-linking increased the delay to first short by 50 percent with respect to the state-of-the-art.

By imposing more stringent requirements on the thermochemical property values of the coat material it would be possible to extend the time further-possibly to the point where no fibers are released in a significant time. Some of the polyimides are envisioned for immediate pursuit when the work is continued. It should be mentioned that considerable experience exists at JPL in the characterization, selection, testing, application, and composite material improvement for various fire needs (Ref. 5).

C. CLUMPING AND PREVENTION OF AIRBORNE FRAGMENTS

This again appears to be an approach novel in the community. This is also the approach that has yielded admirable results. Sodium silicate appears to form a glassy coating when heated. This glassy sheath coalesces the fibers and prevents their release. Even in quantities as small as 2 percent (by weight over the fibers), complete suppression of electrical shorts is seen.

Several other similar coatings should also be pursued. Although the sodium silicate coat appears to meet the requirements of low cost, small departure from state-of-the-art, and ease of handling, there could be other considerations like service life, mechanical properties, and resin compatibility that may demand a different chemical. The hygroscopicity of sodium silicate was mentioned at the Langley Workshop, as requiring further consideration.

---

[5] See footnote 2, p. 6.

D. INSULATION COATINGS

Cladding the fibers in an easily oxidizable metal that becomes an insulator at high temperatures has not been reported in the open literature before. This technique again, has met with full success in that no electrical shorts were observed even over extended periods of time. This success combined with the fact that good electrical conductivity is frequently desired under normal service conditions, makes the cladding technique an extremely attractive subject for further pursuit. Also, as reported in the literature (Ref. 6), the mechanical properties appear to be maintained by the good quality of the aluminum-graphite bond; this is another supporting factor.

E. MECHANICAL PROPERTIES, RESIN COMPATIBILITY, AND SERVICE LIFE

In this brief feasibility effort some of the important secondary questions have not even been tackled. Obviously, the mechanical properties cannot be ignored. Considering that the graphite fiber composites are becoming popular because of their low-weight/high-strength characteristics, any compromise on the mechanical properties will definitely be a drawback. In this connection it is encouraging to note that in a similar composite system, when the fibers were similarly coated for another combustion application, the mechanical properties showed no adverse changes (Ref. 5). The mechanical properties are determined by the bond between the fibers and the resin. Thus it is required that the coat be bonded properly to the fibers and to the resin. In a qualitative manner, the statement can be made that the modified composite materials tested so far did not seem to lose their physical properties.

The thermomechanical properties are also very important. During normal service life a graphite fiber composite may be exposed to temperature excursions in excess of a few hundred degrees Fahrenheit. The differential thermal expansion of the fibers/coat/resin can give rise to severe stresses. These aspects should be investigated. Nevertheless, it is again encouraging that the modified composite materials when burned, showed no evidence of fracture or fissure such as might result from differential thermal expansions.

The resin capability with modified fibers seems to be acceptable. While the actual panel layup and curing are the real tests of the compatibility, a preliminary indication is given by the fact that the castings could indeed be handled. For example, in the earlier study in a different application (Ref. 5), some of the coatings on fiberglass could not even be cast in the epoxy resin systems. No such difficulty was experienced in the present case.

The resin-coat-fiber interface needs careful study in the future, particularly over extended periods of time. This will be pursued in detail when the work is continued.

SECTION VI

RECOMMENDATIONS FOR FURTHER WORK

The objective is to demonstrate feasibility of alleviating the electrical hazards of carbon fiber composites by means of fiber modifications with organic or inorganic chemicals (or both), which include metals and hydrogen-rich substances, before incorporation into the resin. Fiber gasification is the primary purpose of these modifications. This is to be accomplished without adversely affecting the proven good mechanical and low-weight characteristics of carbon fiber composites. It is also the objective to explore at a very low level of effort other avenues that show considerable promise in the main course of these investigations.

The approach will follow the general plan of fundamental analyses, analytical experimentation on components and burn tests on modified composite materials. Different catalysts for graphite gasification will be thermally analyzed after they are coated on the surface of the fibers. The TGA, DSC, and DTA apparatuses will be used. Hydrogen inclusion techniques will be explored. Rapid oxidation of graphite fibers will be studied in some detail. Reported catalysts (Refs. 7 and 8) will be explored as possible means to enhance the kinetic rates of graphite oxidation. The available combustion window bomb at JPL will be used to study the kinetics of graphite oxidation over a range of pressures and temperatures. The combustion rate will be determined through cinematographic observations and pressure and temperature measurements. It is expected that the kinetics scheme may be slightly different from the widely studied schemes of carbon, considering the special physical form (8 μm diameter) and the chemical nature (an outer sheath of graphite and a core of carbon). The oxidation of graphite and carbon was discussed specifically at the Combustion Institute Meeting (WSS/CI, University of Colorado, Boulder, Colorado, April 17-18, 1978) where some of the leading authorities on the subject assembled. The available studies on oxidation of ring-structured carbon chemicals will be used as a basis for the study of catalytic oxidation. Schemes will be explored for converting the outer sheath of graphite to carbon at high temperatures for easier oxidation. All of these schemes will be explored with a thermochemical model, which will allow study of the basic processes at a fundamental level. Hydrogen adsorbing metals such as palladium and zirconium will be sputtered onto the graphite fibers in a thin coating. Work will specifically explore the etching of graphite fibers to obtain the desired hydrogen inclusion without this addition of metal. A proton gun will be used in an attempt to implant hydrogen in depth in the fibers rather than on the surface alone. The hydrogenated fibers will be tested for burn rates at different times after the treatment to see if there is loss of hydrogen. In the event hydrogen loss is detected, the hydrogenated fibers will be clad in metals to contain the hydrogen. The hydrogenated fibers will be impregnated with one or more of the standard resins (e.g., epoxy, polyimide, and phenolic) in the requisite proportions. Panels will be prepared by laying up the treated fiber cloth using the hot press at JPL. The cure time-temperature combination will be chosen carefully so as not to adversely affect the catalyst and hydrogen treatment. The panels so prepared will be burned in the test apparatus, that needs some

improvements from its present form. The time for the first short will be used as an index for rating the different treatments. The data gathered will be used as a guide in formulating improved fiber treatments. Mechanical properties of the modified composite materials will be tested in the standard ASTM recommended techniques available at JPL. The ageing properties that determine the service life of the composite will be determined in the accelerated ageing study apparatus available for propellant research at JPL.

The data gathered will be reviewed to determine the ease of commercial implementation of the best technique evolved. Contacts will be made with outside industry to assess their view on the ease of commercialization. Any modifications needed to aid commercialization will be studied in detail. The samples prepared will then be sent to other test centers for their evaluation. The final selection will be available for a demonstration to industry, universities, and research institutions at the end of this phase of work.

Considering the prevailing uncertainties in the general field of heat transfer and thermochemistry in such complex materials, a low-level effort will be devoted to thermochemical modeling of the key processes to guide our experiments.

REFERENCES

1. A Report of Observed Effects on Electrical Systems of Airborne Carbon/Graphite Fibers, NASA Technical Memorandum 78652, National Aeronautics and Space Administration, Washington, D.C., January 1978.

2. United States Department of Commerce News ITA 78-13, Department of Commerce, Washington, D.C., January 20, 1978.

3. "Peril from Superplastics?" Time, March 13, 1978.

4. Gibbs, H.H., et al., "Carbon Fiber Structure and Stability Studies" Society of the Plastics Industry, Reinforced Plastics Meeting, Washington, D.C., February 1978.

5. Ramohalli, Kumar N. "A Concept for Improved Fire-Safety through Coated Fibers", Western States Section of the Combustion Institute paper 77-16 Spring Meeting, Seattle, Washington, April 1977.

6. The United Kingdom Symposium on Aluminum Graphite Composites. Carbon Fibers, their Composites and Applications, International Conference, February 2-4, 1971, The Plastics Institute, 11 Hobar Place, London SW1.

7. Baker, R. T.K. et al., "Controlled Atmosphere Electron Microscopy Studies of Graphite Gasification - The Catalytic Influence of Vanadium and Vanadium Pentoxide", Carbon, Vol. 13, pp. 141-145, 1975.

8. Baker, R. T.K., and T. Skiba, Jr., "The Behaviour of Silver Particles Supported on Graphite in Various Gaseous Environments", Carbon, Vol. 15, pp. 233-237, 1977.

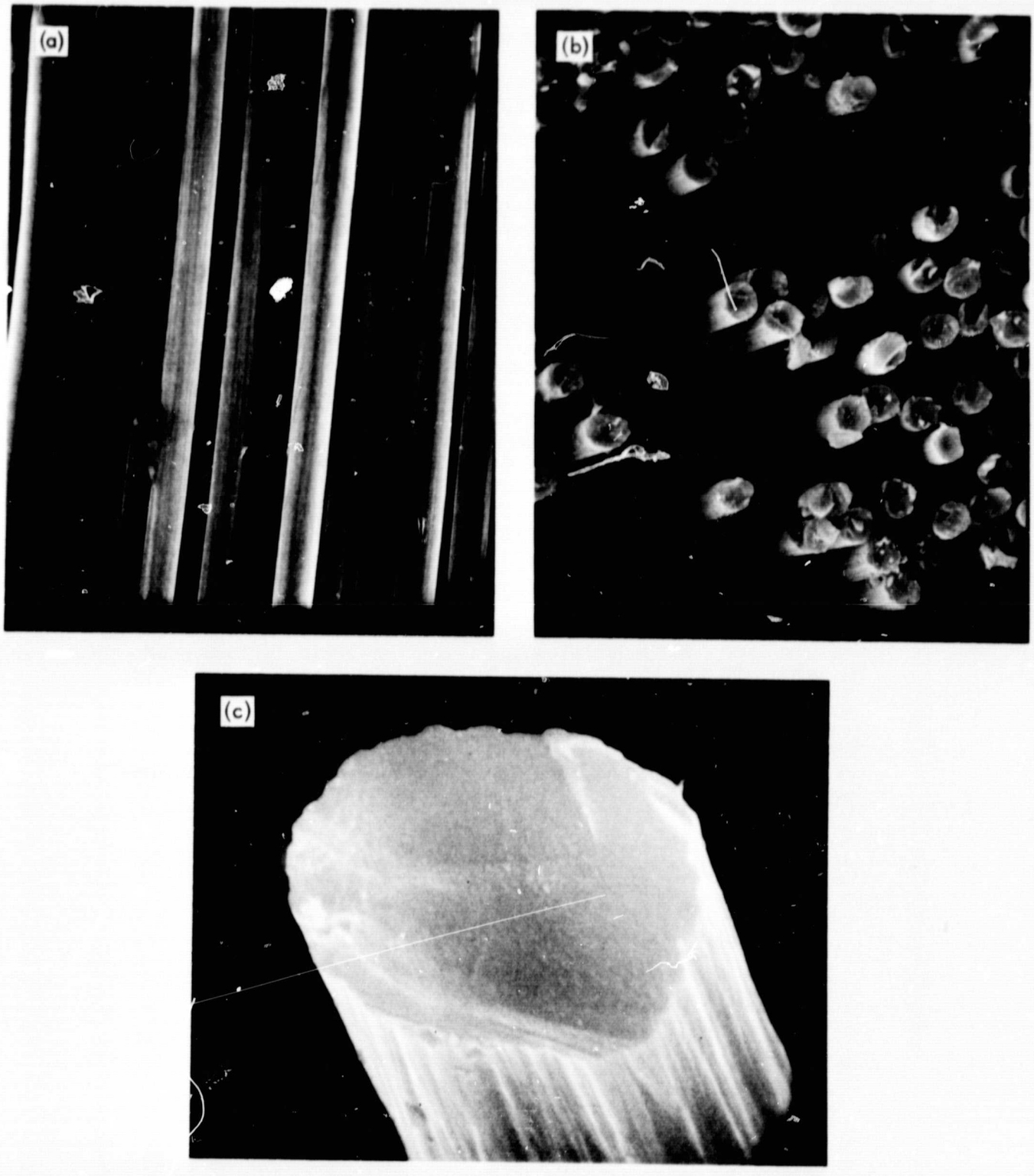


Fig. 1. Three views of Thornel-300 under the scanning electron microscope: (a) and (b), 1000x; (c) 10,000x

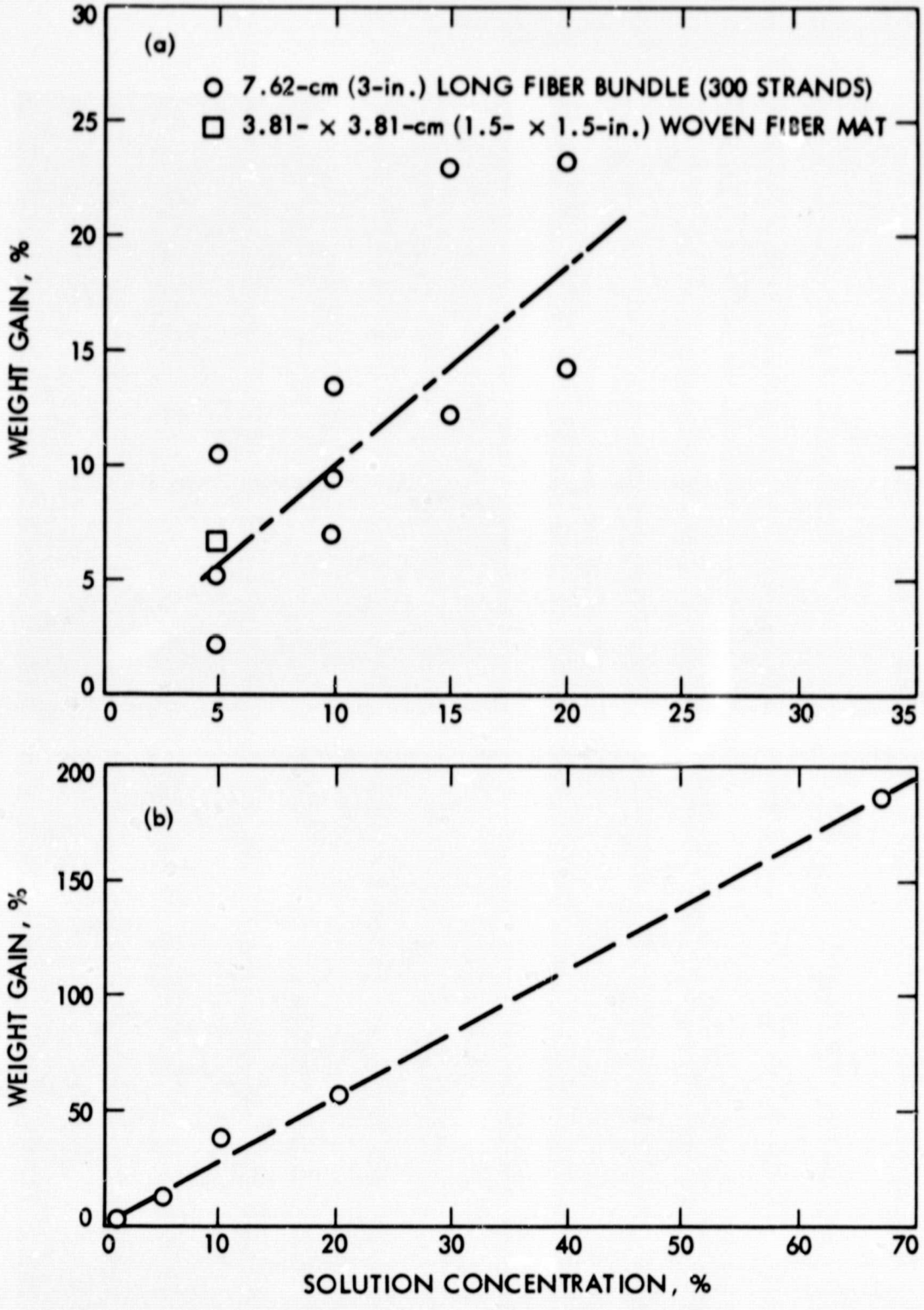


Fig. 2. Weight gain of Thornel-300 fibers as a function of solution concentration: (a) sodium silicate solution; (b) Control-64 solution

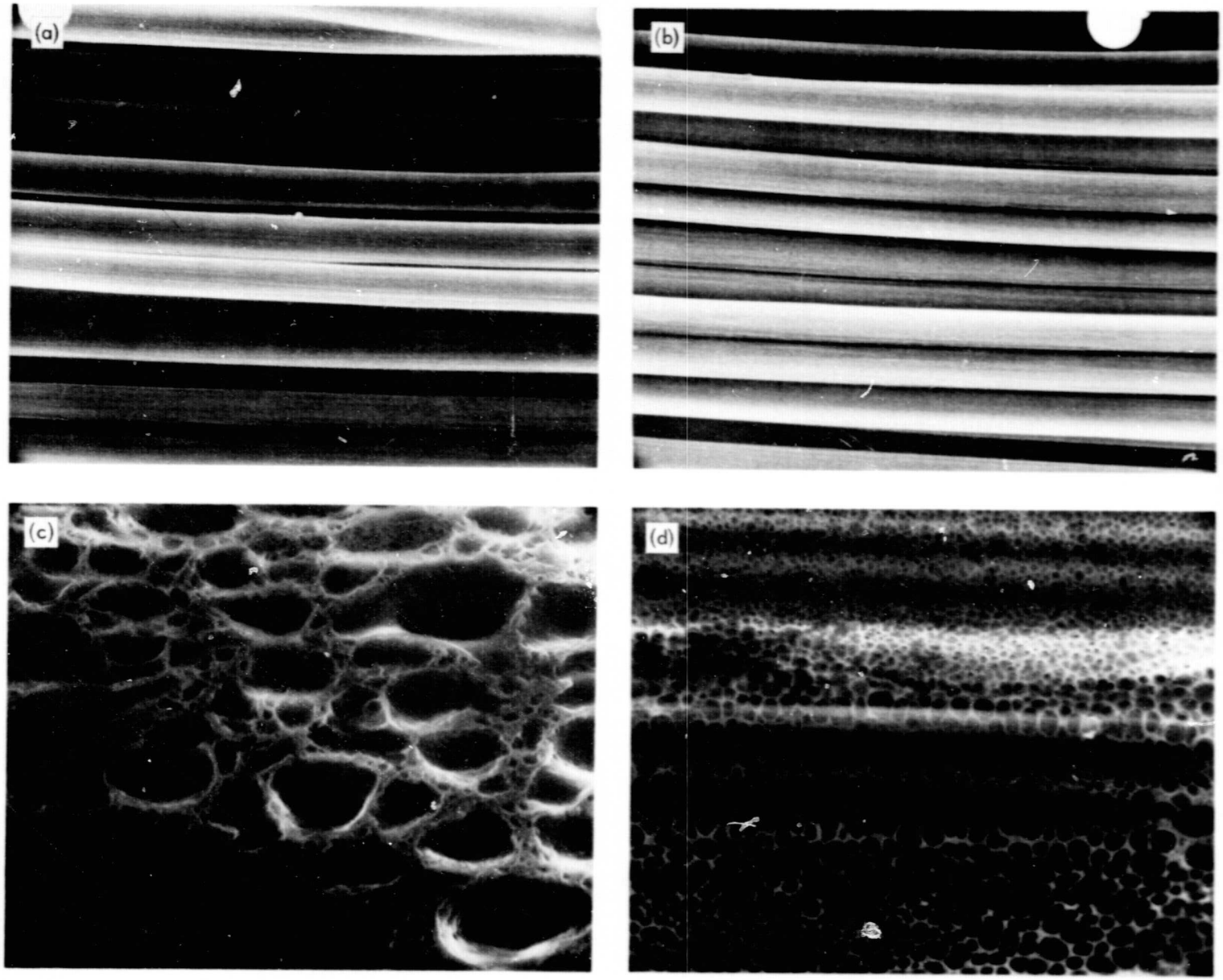


Fig. 3. Improvement in surface wettability of Thornel-300 (to coat EC + TCP) by exposure to an argon plasma for 30 minutes at 133.3 N/m^2 (1 torr): (a) uncoated before exposure, (b) uncoated after exposure, (c) coated before exposure, (d) coated after exposure

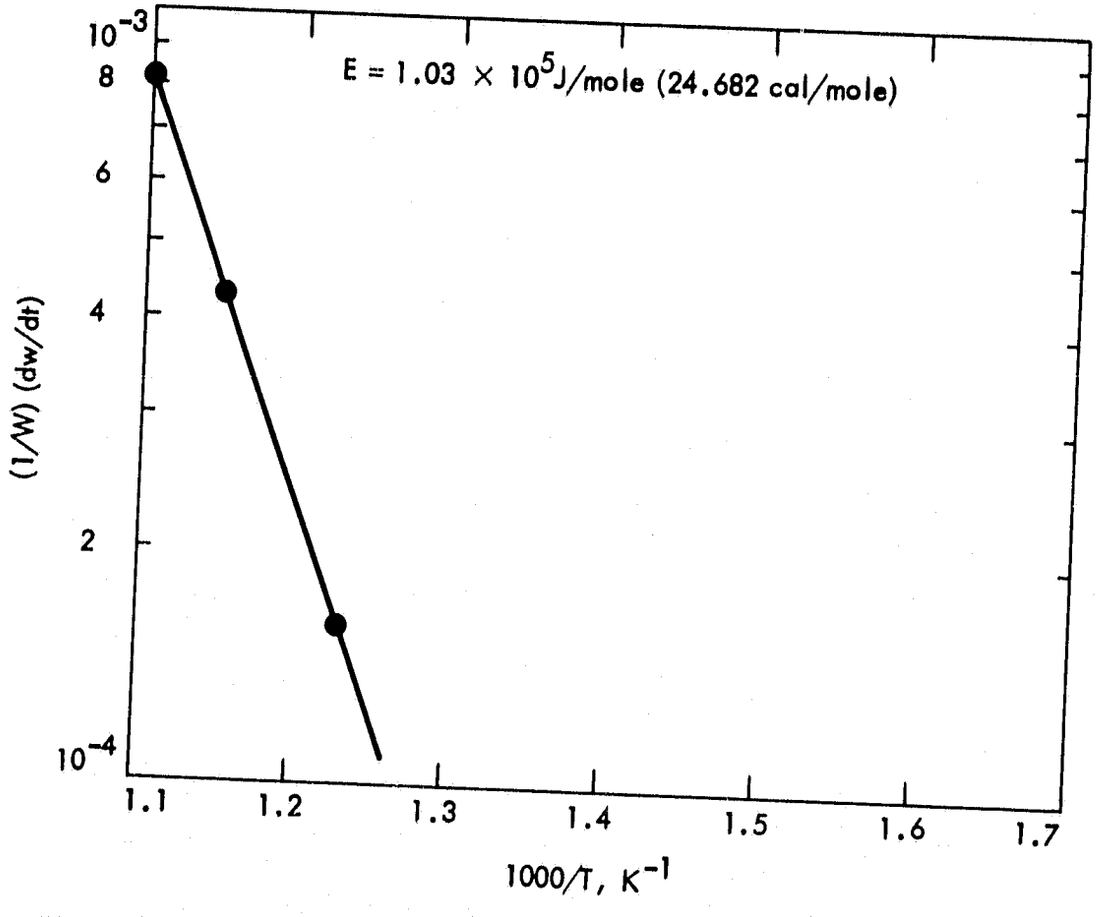


Fig. 4. Reduction of TGA data for the kinetic constants

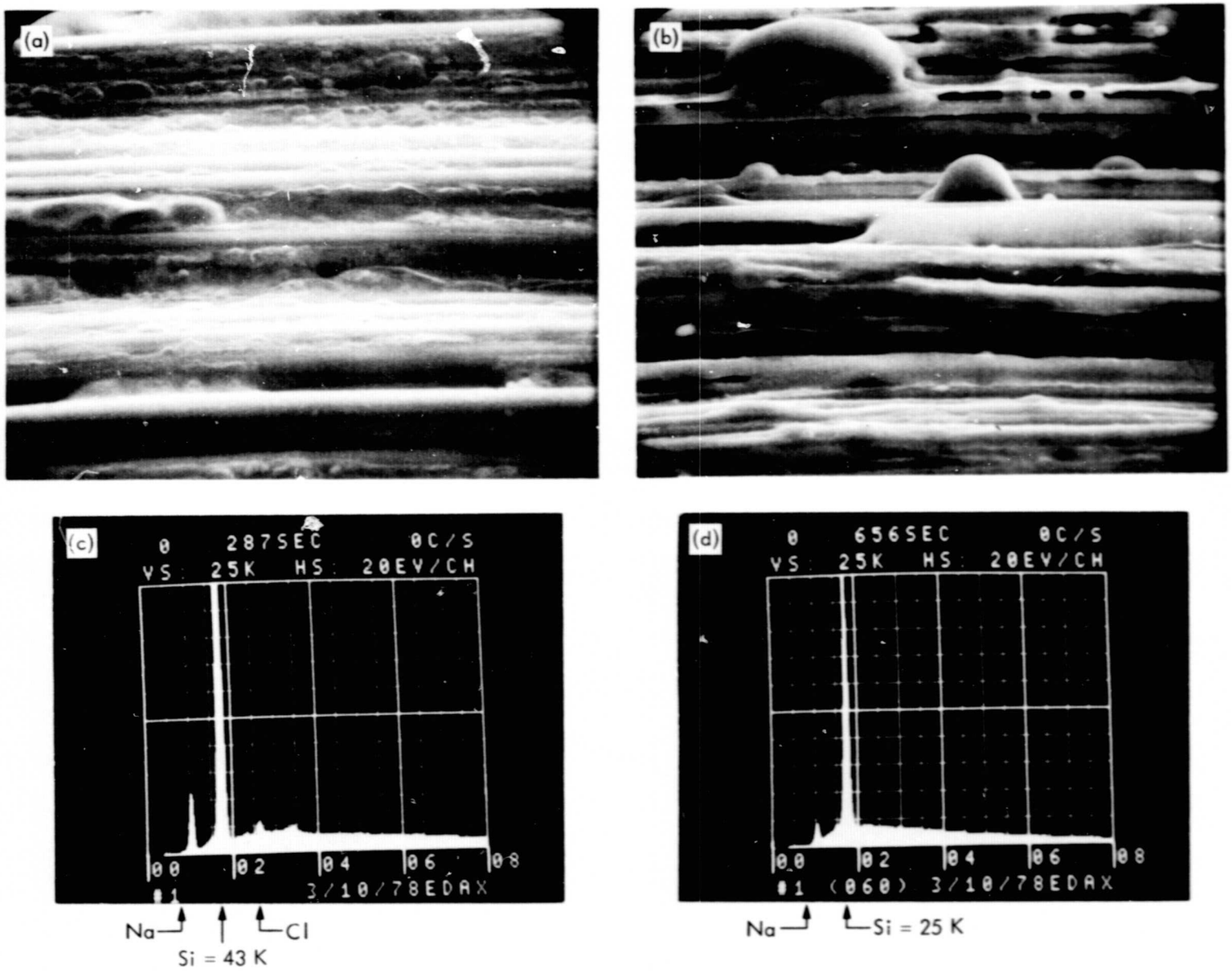


Fig. 5. The clumping mechanism of Thornel-300 fiber with sodium silicate coating: (a) before burning, 1000x; (b) after burning, 1000x. X-ray spectra (c) before and (d) after exposure to flame. The percent coat shown (13.7%) is much higher than the typical value of 2 to 3%

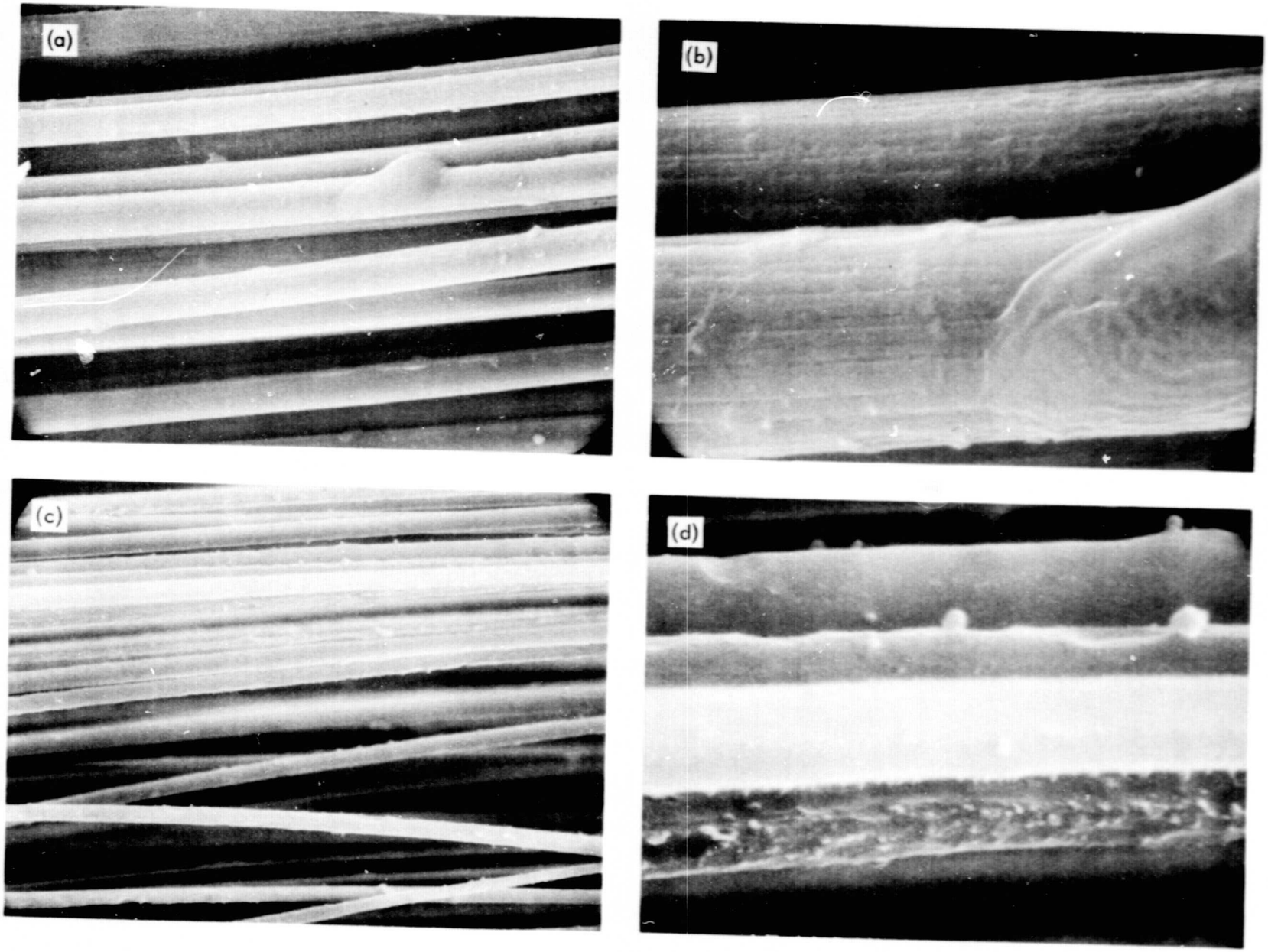


Fig. 6. The mechanism of Thornel-300 fiber clumping the coating (3.5%) of Control-64: unburned fibers (a) 1000x, (b) 5000x; fibers after 30-s exposure to flame (c) 1000x, (d) 5000x

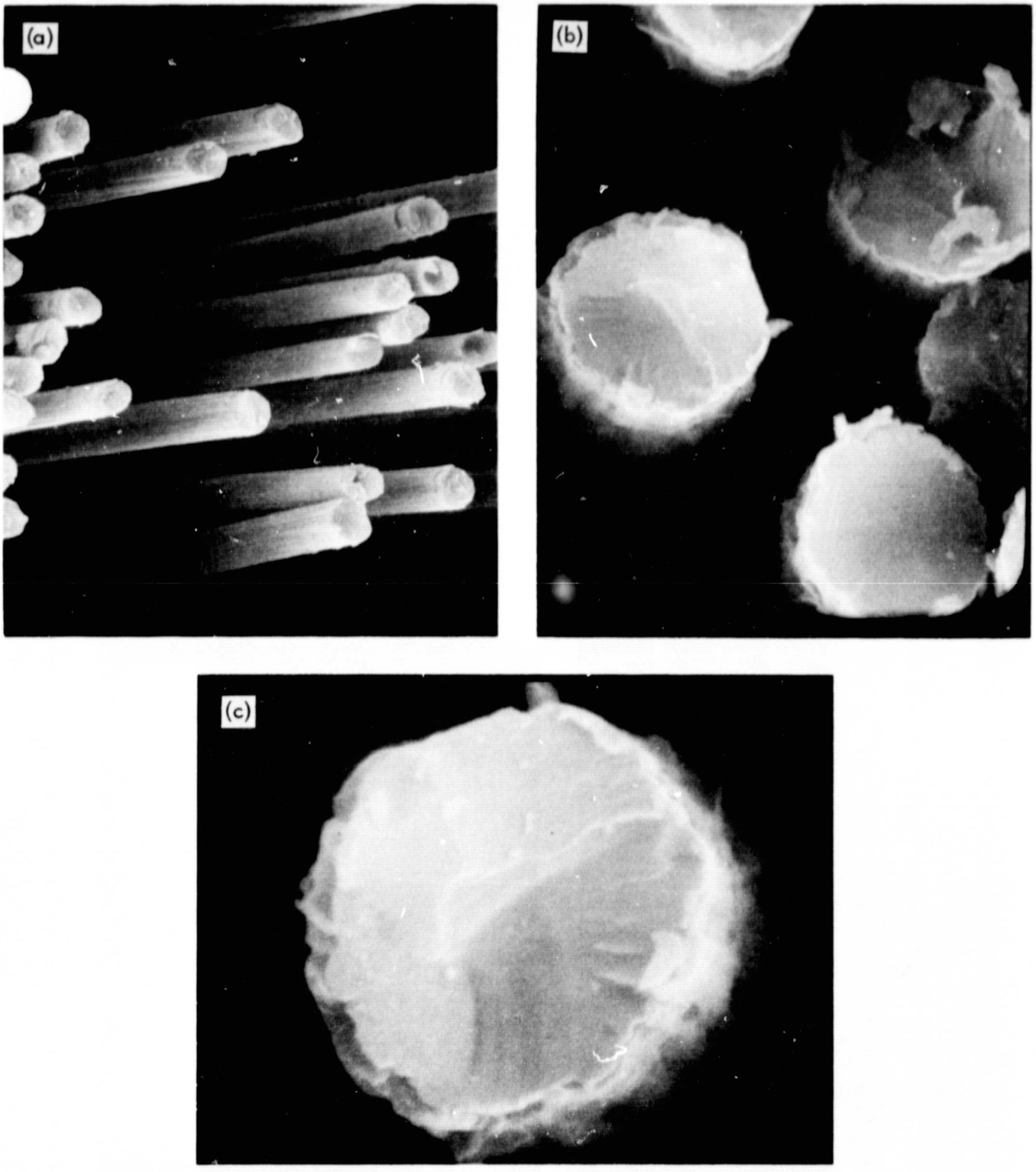


Fig. 7. Aluminum cladding on Thornel-300; note the thin coat on the 8-micron fibers: (a) 1000x, (b) 5000x, (c) 10,000x

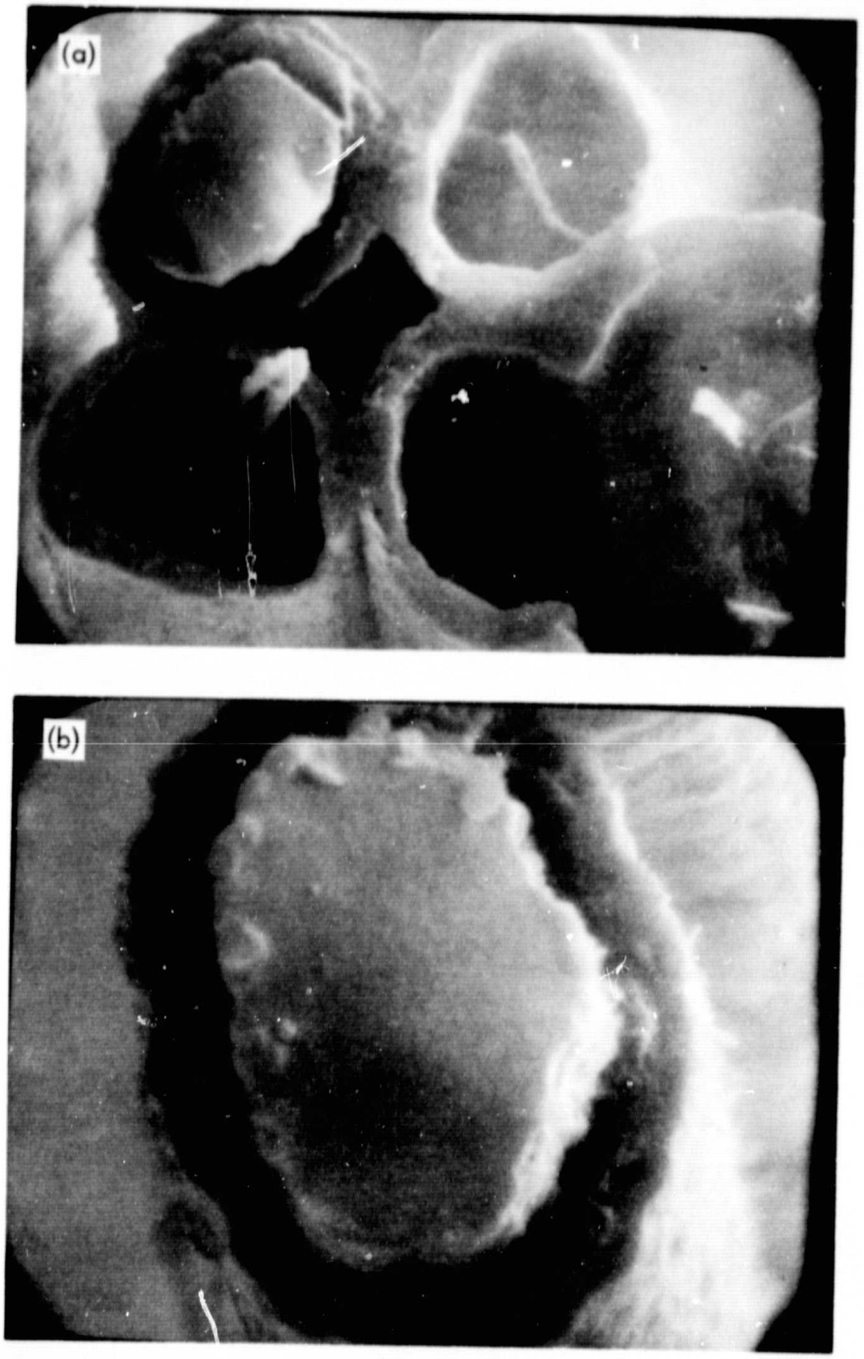


Fig. 8. Aluminum-clad Thornel-300 after burn tests; note the aluminum-oxide coating on the fibers: (a) 5000x; (b) 10,000x

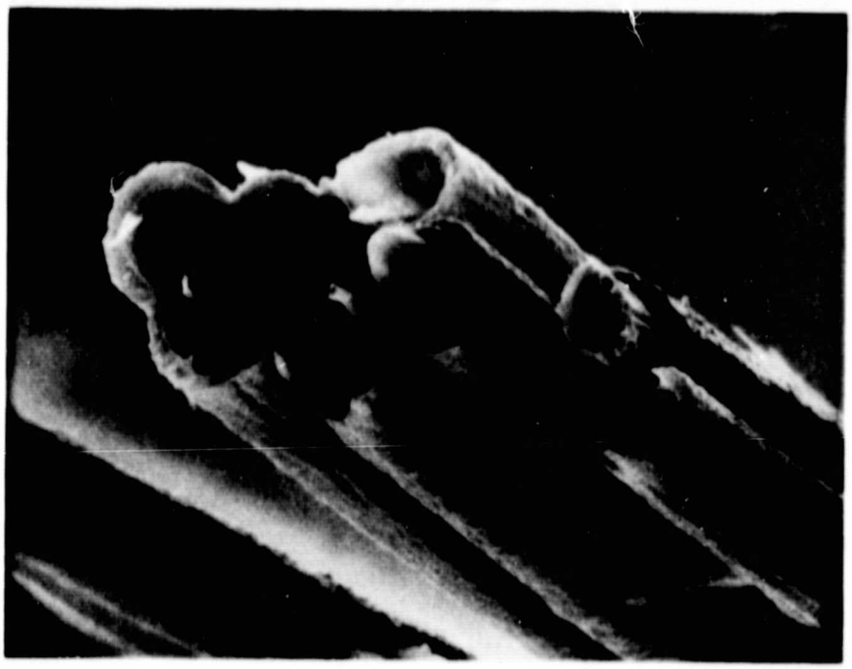


Fig. 9. The desirable retention of an aluminum-oxide coat on the fiber even after the fiber is consumed implies superior mechanical properties

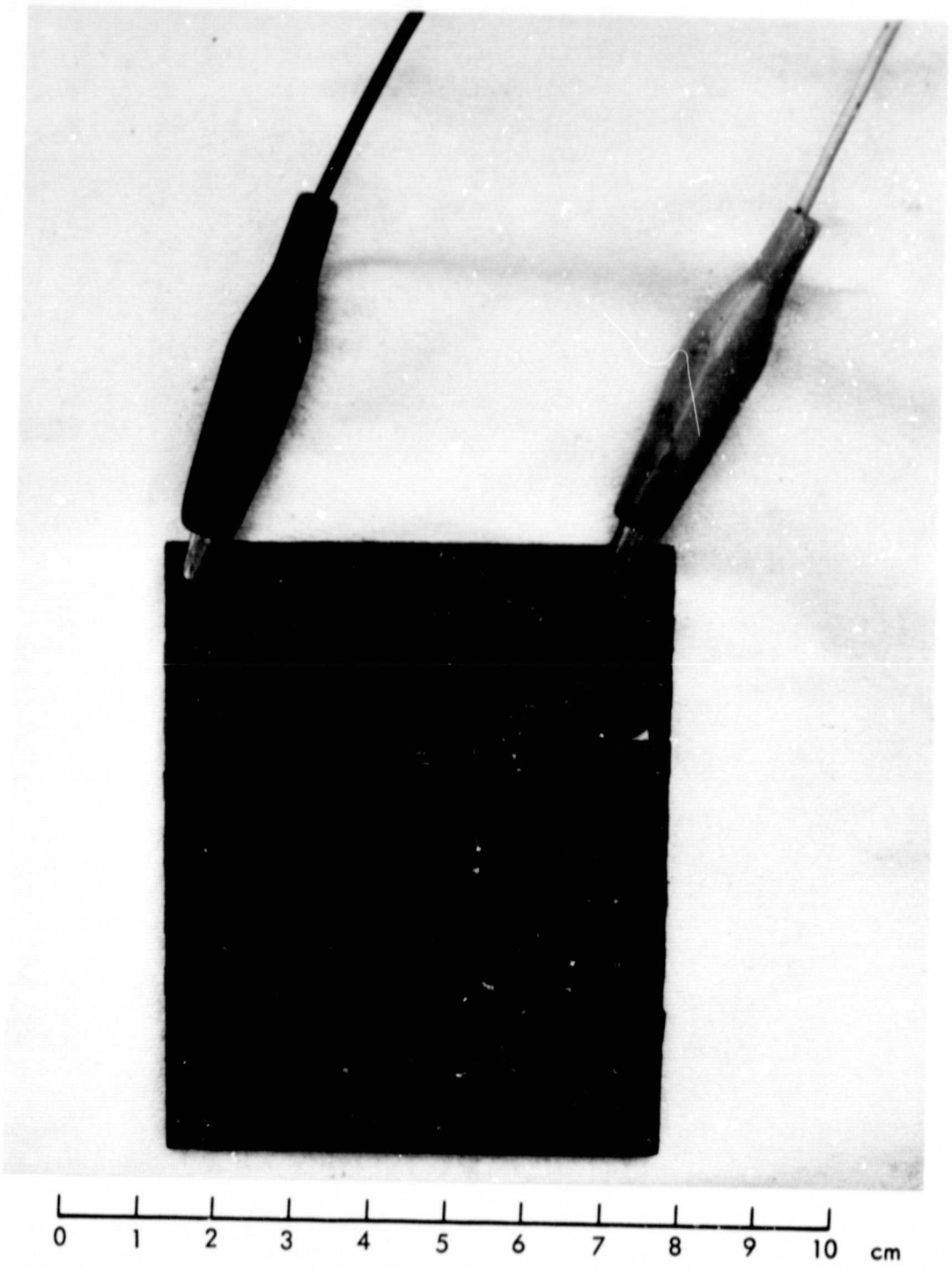


Fig. 10. The first design of a typical circuit board for exposure to carbon fiber composites during a fire; copper strips are bound to masonite board

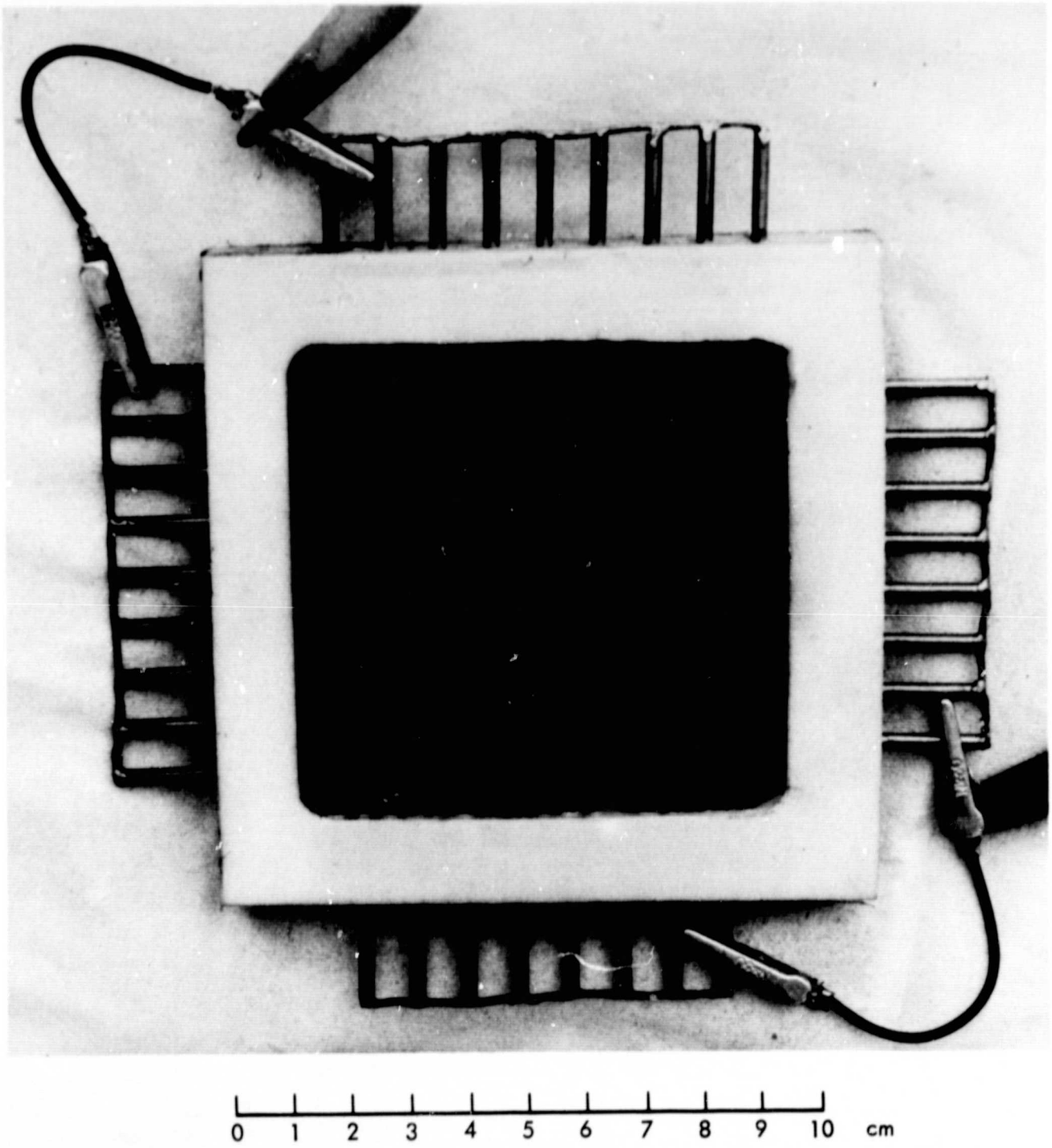


Fig. 11. Improved design of the circuit board for exposure to burning carbon fibers; the design allows soot to pass freely through, rather than settle on the board

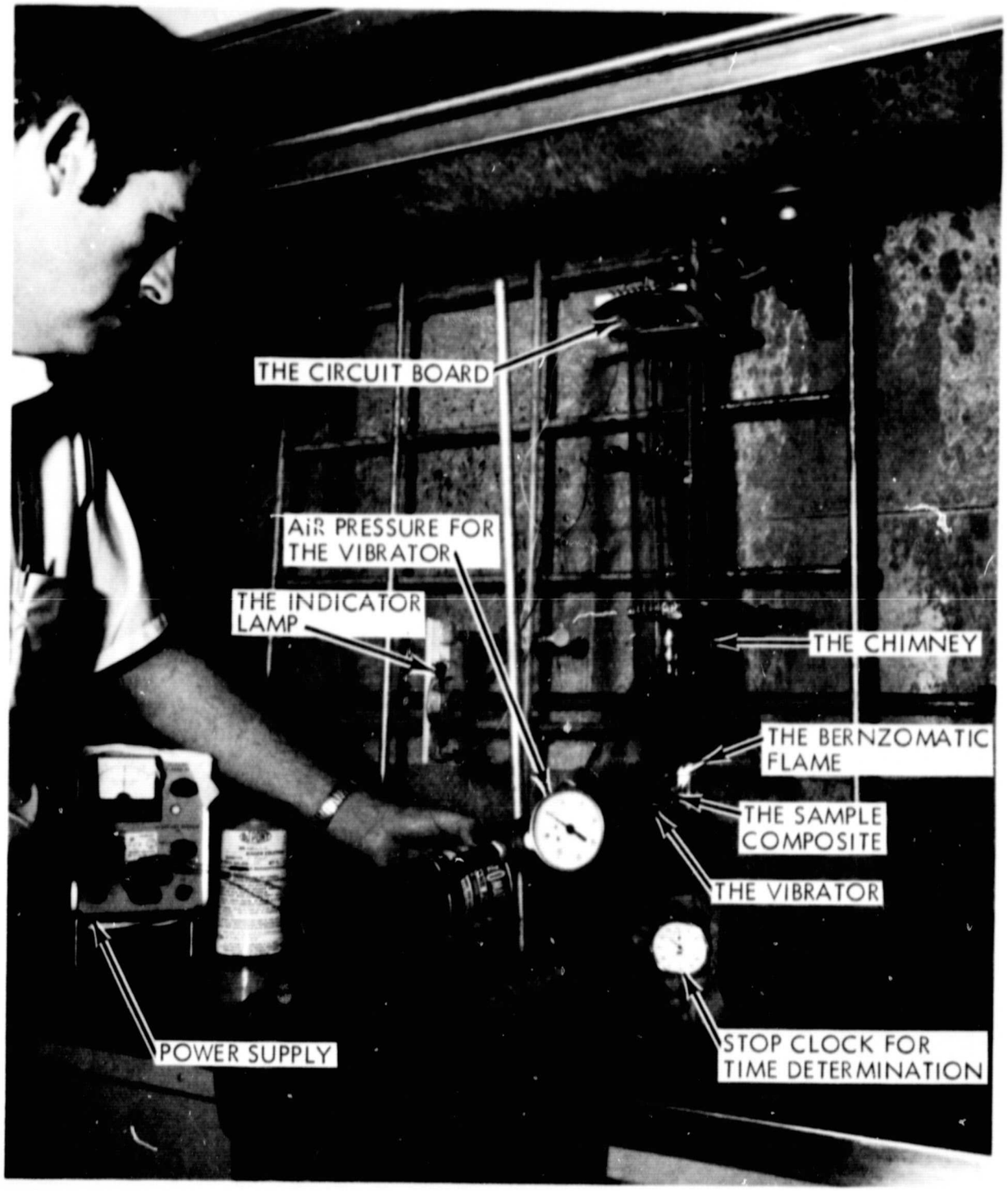
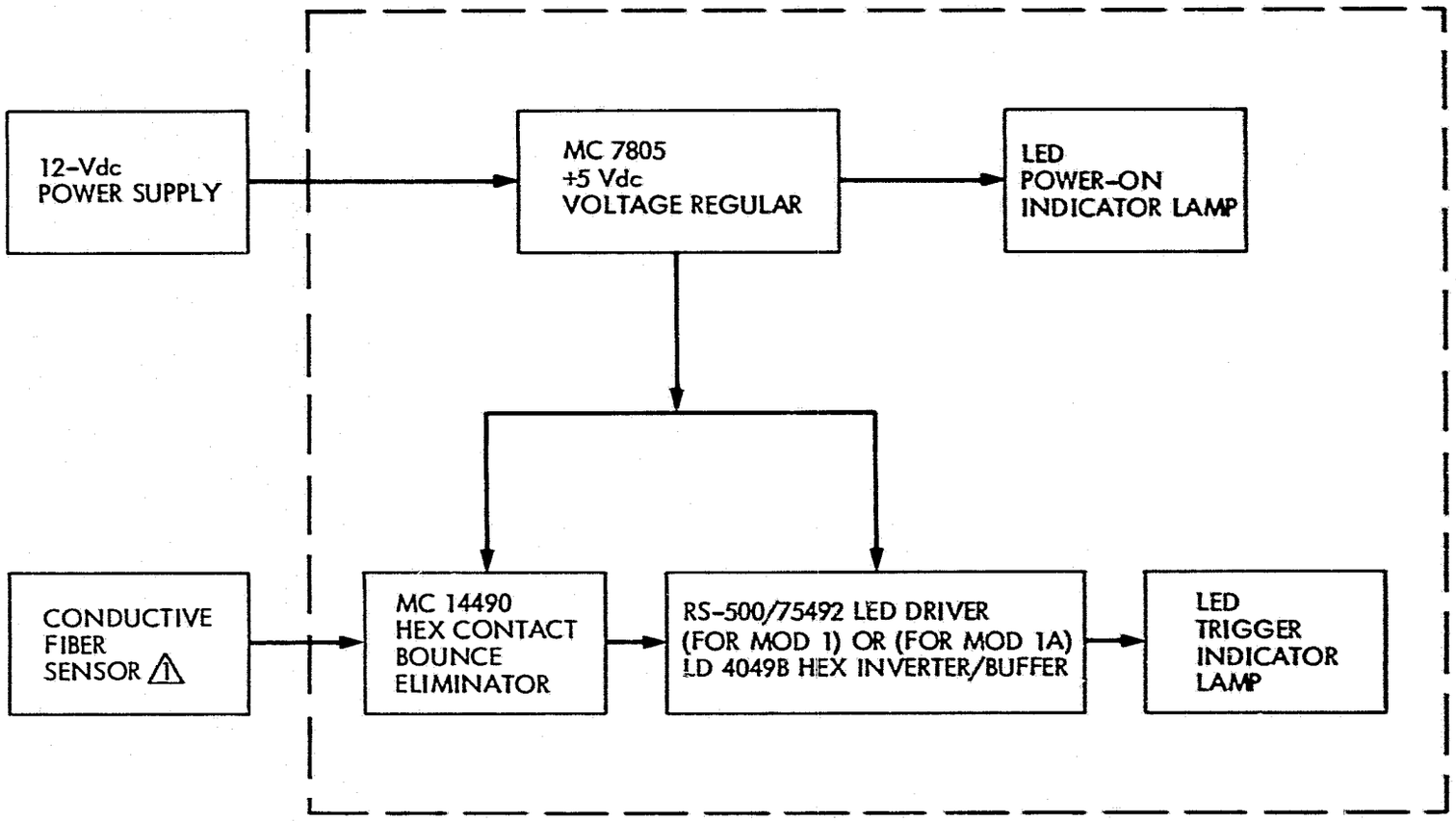


Fig. 12. Test apparatus used to determine the electrical shorting characteristics of burning graphite-fiber and modified graphite-fiber composites



⚠ TWO MODELS OF SENSORS SHOWN IN FIG. 10 AND FIG. 11

Fig. 13. Block diagram of conductive fiber sensor and Models 1 and 1A detector circuit

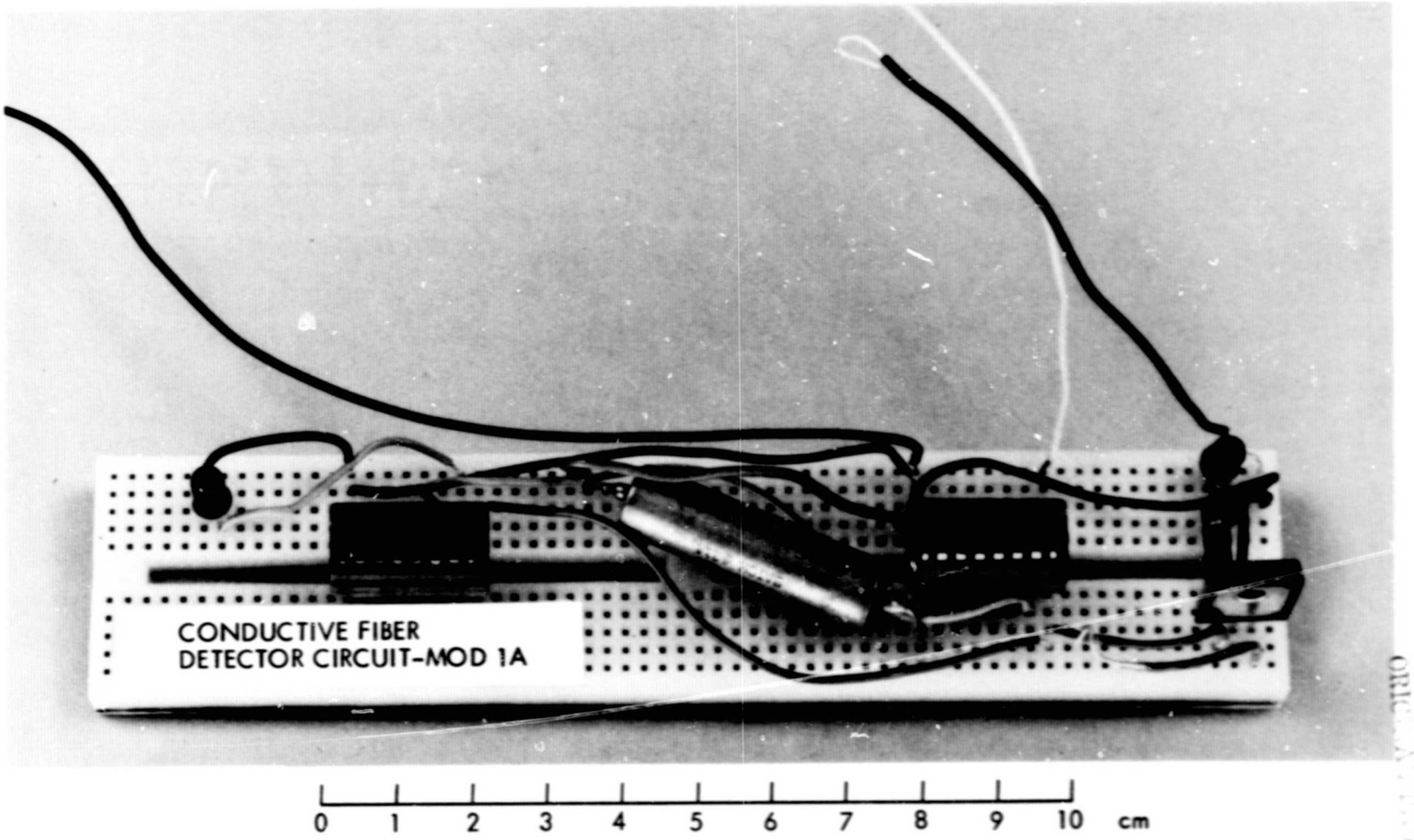


Fig. 14. Model 1A detector circuit breadboard

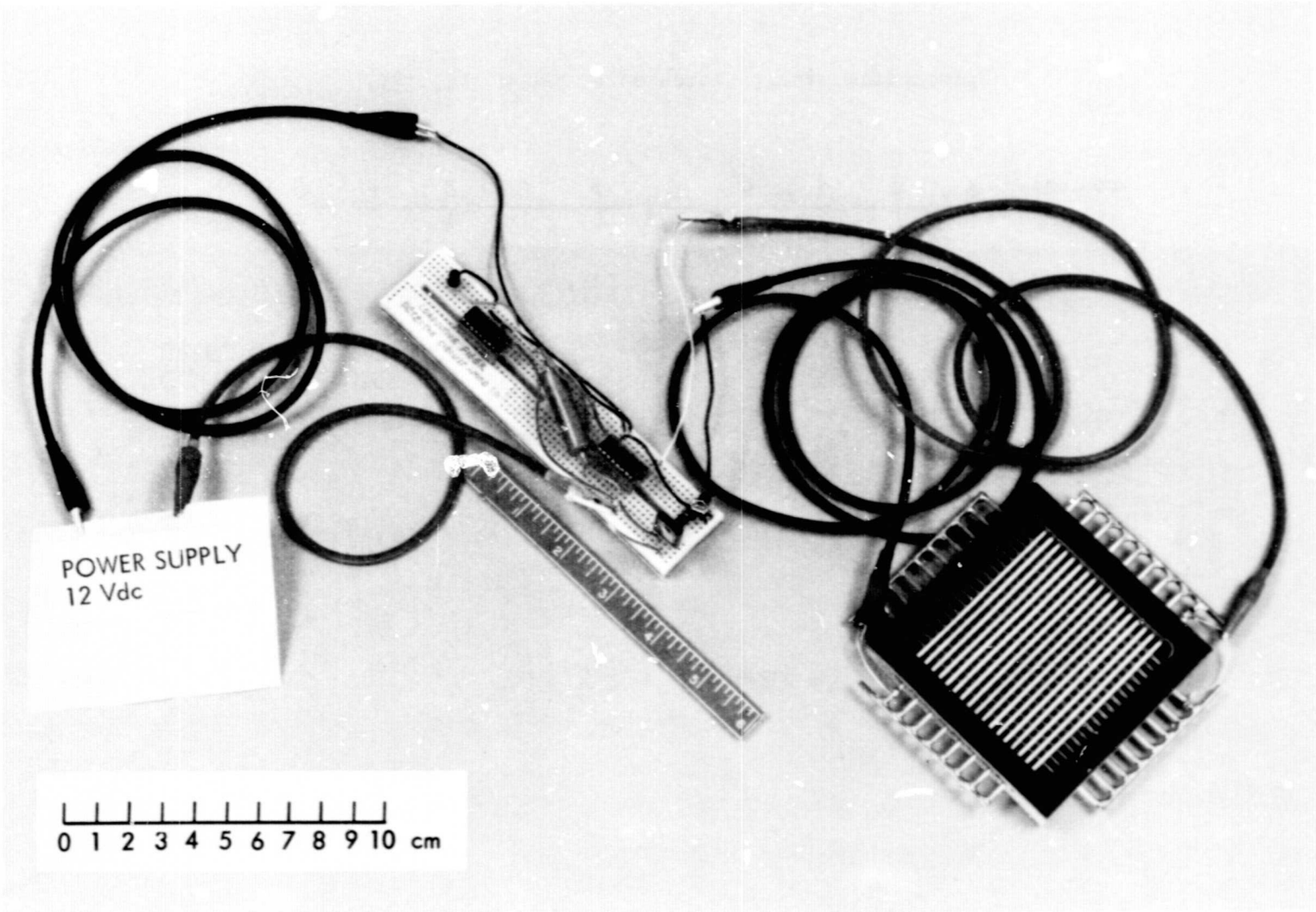
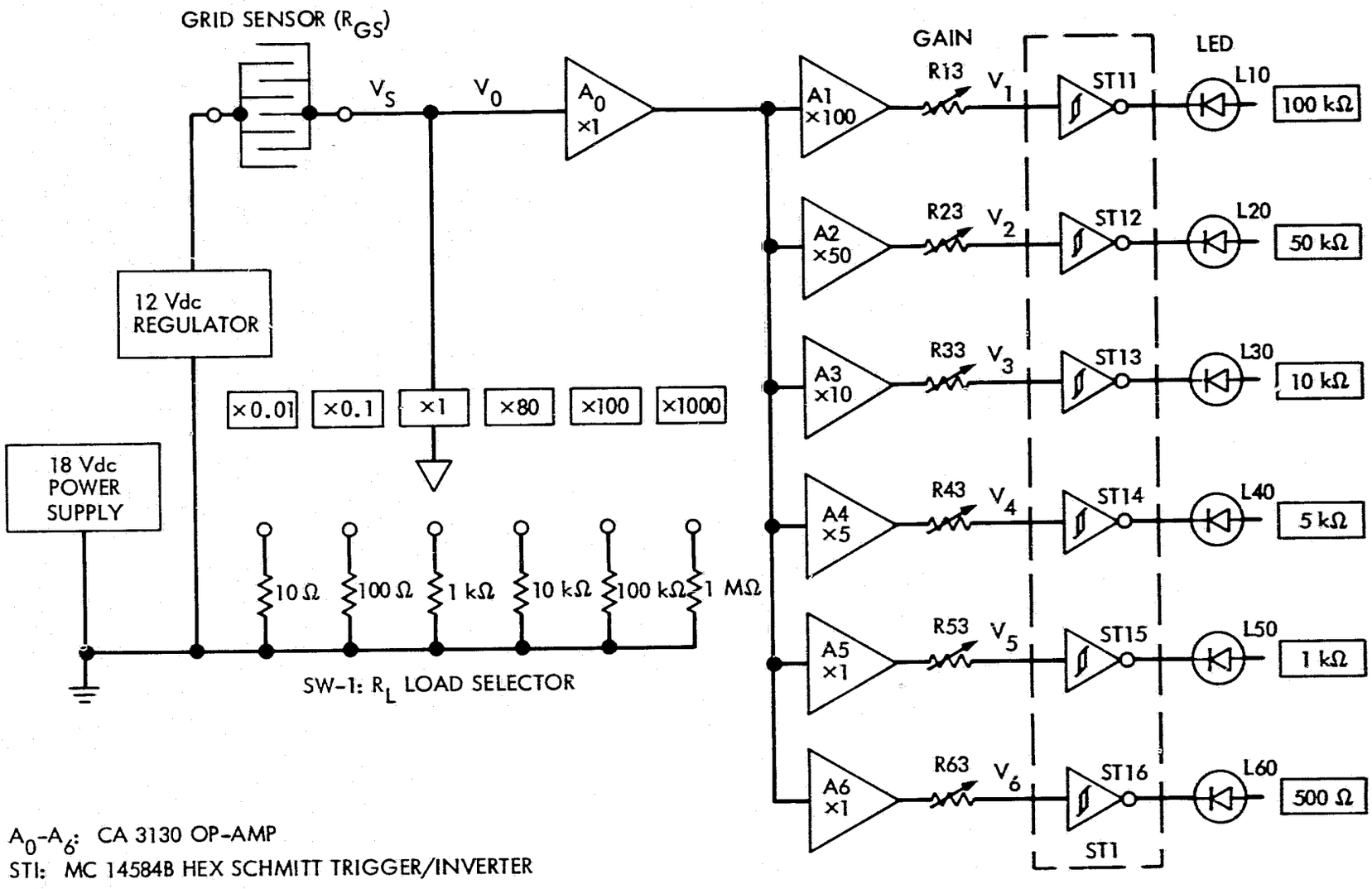


Fig. 15. Model 1A breadboard and Model 2 sensor



A_0-A_6: CA 3130 OP-AMP
ST1: MC 14584B HEX SCHMITT TRIGGER/INVERTER

Fig. 16. Schematic diagram of conductive fiber sensor and Model 2 detector circuit

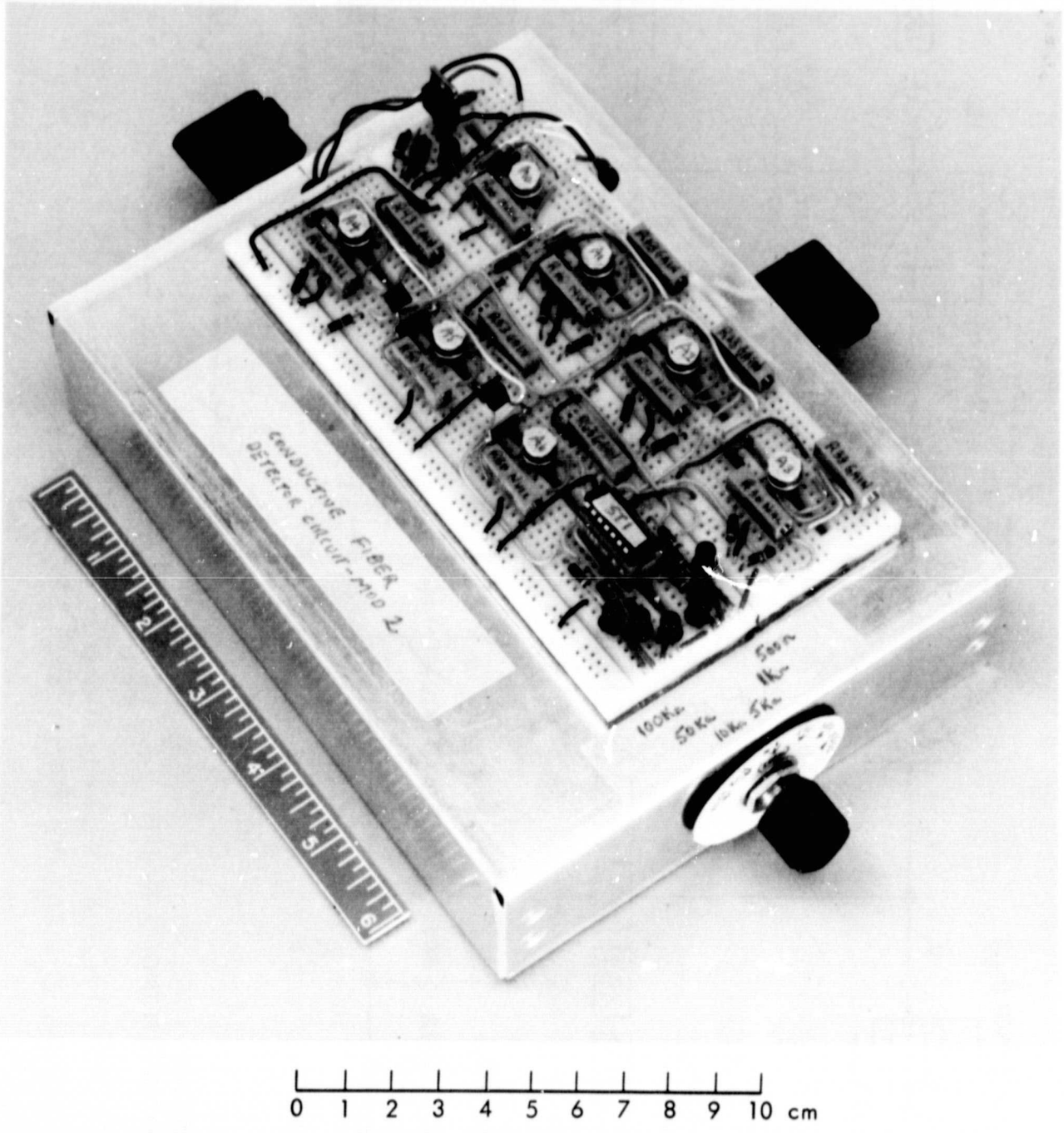


Fig. 17. Model 2 detector circuit breadboard

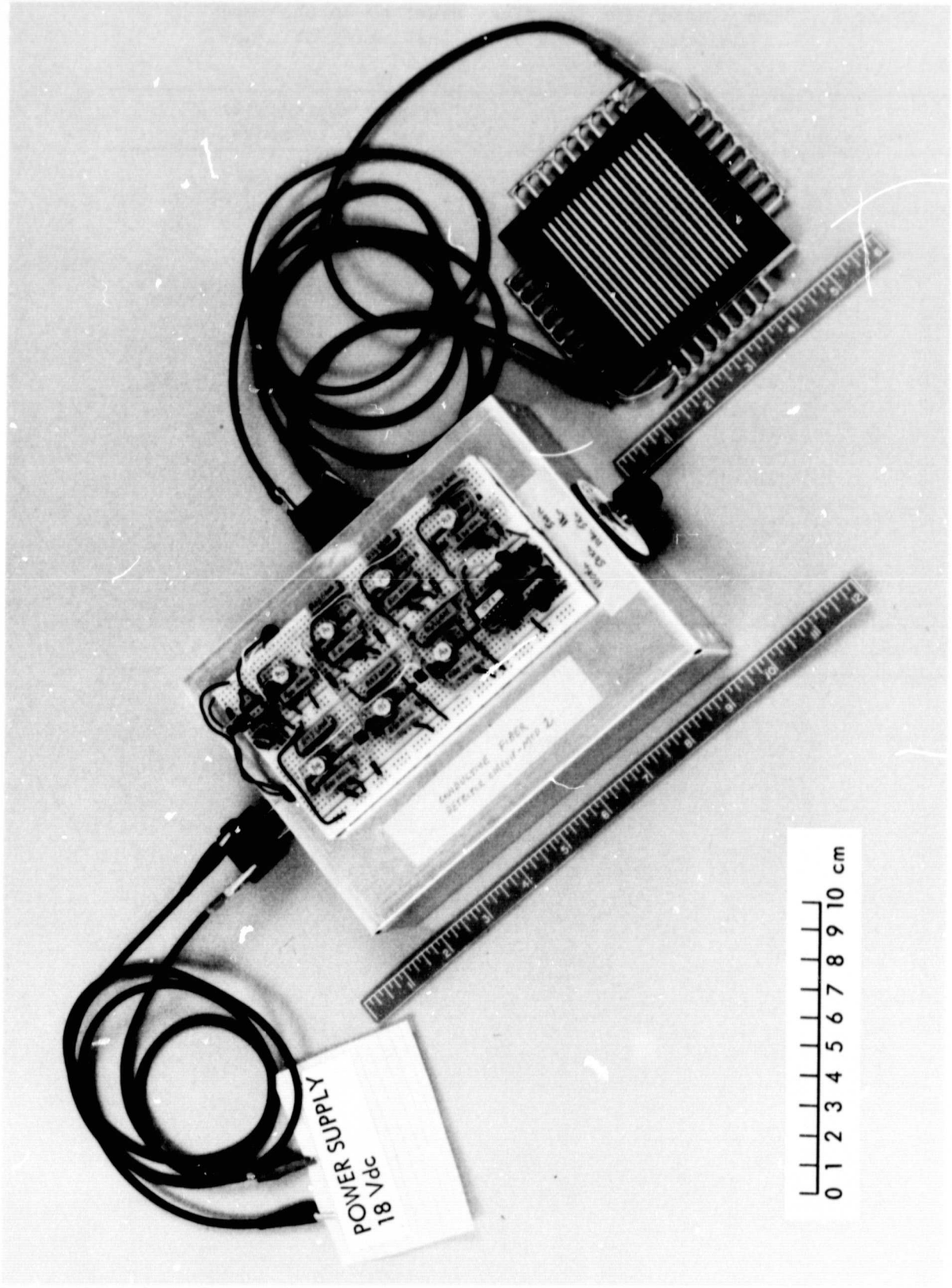


Fig. 18. Model 2 breadboard and Model 2 sensor

Table 1. Time elapsed for the first short to be observed in the test apparatus since initiation of flame.

Untreated fiber in epoxy, s	Fibers coated with EC and ECP in epoxy, s
55[a]	22
15	21
5	22
12	12
15	22
10	18
10	19
20	21
14	20.5

[a]This was the very first test and there could be some uncertainty.

APPENDIX

SAMPLE TGA DATA SHEETS

Examples of TGA data similar to that used to derive Fig. 4 are presented on the following raw data sheets.

TGA DATA SHEET

Run No: 47 Date: 4-4-78

Sample Type Carbon fiber coated with Pd + H_2

Initial Sample Wt 0.93 mg Final Sample Wt. 0.026 mg

Recorder Range 1 mg Chart Speed 10 mm/min

Chart Range 1 mg Scan Speed 20°C/min

Purge Atmosphere Air Flow Rate 30 cc/min

Operator F.W.T.

Reduced Data

Temperature, °C	% Wt. Loss	Remarks
100	1.18	
200	1.93	
300	2.97	
400	5.38	
500	38.71	
600	96.24	
700	97.20	

TGA DATA SHEET

Run No: 49 Date: 4-4-78

Sample Type Carbon fiber coated with Pd + H_2

Initial Sample Wt. 0.800 mg Final Sample Wt. 0

Recorder Range 1 mg Chart Speed 10 mm/min

Chart Range 1 mg Scan Speed 20°C/min

Purge Atmosphere Air Flow Rate 30 cc/min

Operator F.W.T

Reduced Data

Temperature, °C	% Wt. Loss	Remarks
100	0.57	
200	1.61	
300	2.87	
400	4.94	
500	32.76	
600	98.06	
700	99.77	
800	100.00	

TGA DATA SHEET

Run No: 53 Date: 4-4-78

Sample Type Carbon fiber coated with Pd + H_2

Initial Sample Wt. 0.998 mg Final Sample Wt. 0.805 mg

Recorder Range 1 mg Chart Speed 10 mm/min

Chart Range 1 mg Scan Speed 20°C/min

Purge Atmosphere N_2 Flow Rate 30 cc/min

Operator F.W.T

Reduced Data

Temperature, °C	% Wt. Loss	Remarks
100	0.50	
200	1.30	
300	2.01	
400	3.01	
500	4.51	
600	6.21	
700	9.02	
800	12.33	
900	15.53	
1000	19.34	

NASA—JPL—Coml., L.A., Calif.